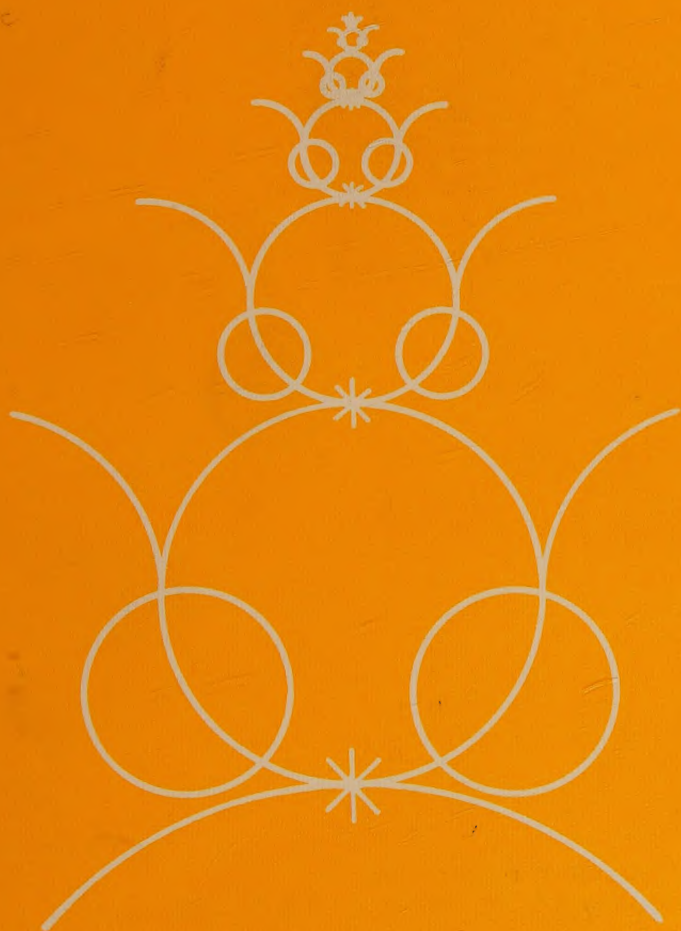


THEORIES OF CHEMICALLY INDUCED MAGNETIC POLARIZATION

J. BOLDEN PEDERSEN



ODENSE UNIVERSITY PRESS 1979

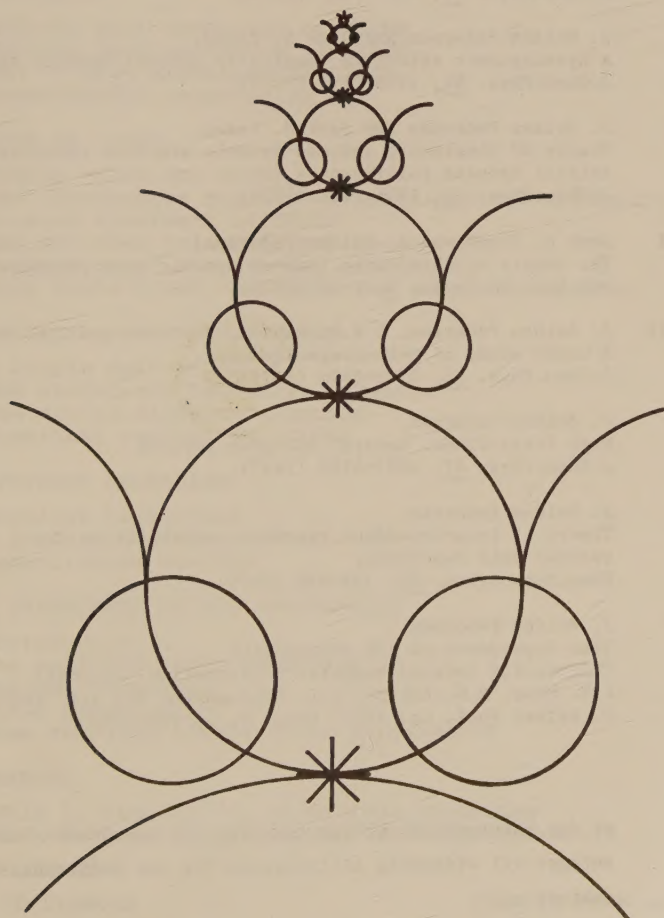


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- III J. Boiden Pedersen,
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- IV J. Boiden Pedersen and Jack H. Freed,
Some theoretical aspects of chemically induced dynamic
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A hydrodynamic effect on chemically induced dynamic spin polarization.
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- VI J. Boiden Pedersen and Jack H. Freed,
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Initial triplet polarization.
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- VII Jack H. Freed and J. Boiden Pedersen,
The theory of chemically induced dynamic spin polarization.
Adv.Magn.Resonance 8, 1-84 (1976).
- VIII J. Boiden Pedersen, C.E.M. Hansen, H. Parbo and L.T. Muus,
A CIDEP study of p-benzoquinone.
J.Chem.Phys. 63, 2398-2405 (1975).
- IX J. Boiden Pedersen,
High field CIDNP. General analytic results.
J.Chem.Phys. 67, 4097-4102 (1977).
- X J. Boiden Pedersen,
Theory of spin-dependent reaction probabilities for
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PREFACE

This monograph presents a discussion of the theories of chemically induced magnetic polarization developed in eleven papers [I-XI] listed elsewhere. The presentation is written with the intention of making the subject more accessible to scientists who are not already experts in the field. For that reason the physical pictures and the basic models are emphasized. Furthermore, each chapter begins with a qualitative discussion meant to facilitate the understanding of the results obtained by the quantitative theories [I-XI]. These theories are given in outline only whereas the most important and general results are presented and discussed.

The work has been carried out at the Department of Chemistry, Cornell University, at the Department of Chemistry, Aarhus University, and at the Department of Physics, Odense University, in the period from February 1972 to June 1978. The work has been supported by a NATO research grant and by Statens naturvidenskabelige forskningsråd.

I am pleased to acknowledge the fruitful collaboration with Professor J.H. Freed. His enthusiasm and our numerous discussions have been an intense inspiration to me. I am also very indebted to Professor L.T. Muus for his constant advice and help.

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Odense, June 1978.

Jørgen Boiden Pedersen

1

INTRODUCTION

Chemically Induced Magnetic Polarization is the name given to the generation of non-equilibrium populations of electron and nuclear spin levels induced by chemical reactions. The nuclear effect is called CIDNP (chemically induced dynamic nuclear polarization) and the electronic effect is called CIDEP (chemically induced dynamic electron polarization). The effects were discovered by magnetic resonance spectroscopy [1-3] and are manifested by ESR and NMR lines with transient anomalous intensities. Fig. 1 illustrates the CIDNP effect; it shows two NMR spectra of a compound produced by a reaction recorded respectively while the reaction is going on (1A) and after completion of the reaction (1B). The spectrum (1A) has some lines in emission (E) and others in enhanced absorption (A).

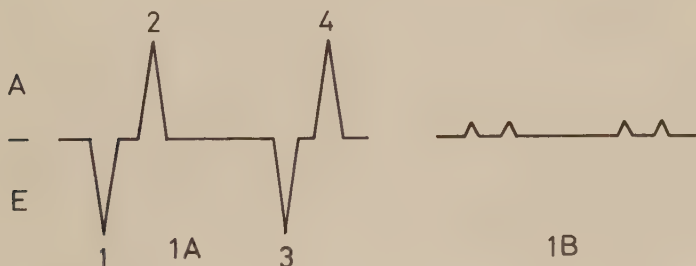


Fig. 1. NMR spectra of a compound produced by a reaction; (1A) is recorded during the reaction; (1B) after completion of the reaction. Emission and absorption are indicated by E and A.

The intensity enhancement caused by the CIDNP effect, i.e. the line intensity in Fig. 1A relative to the equilibrium intensity in 1B, may be of the order of one thousand.

The CIDEP effect on the ESR spectrum is much smaller than the corresponding CIDNP effect on the NMR spectrum. Generally, the intensity enhancements are of the order of unity in steady state spectra such as that displayed in Fig. 2. However, intensity enhancements of the order of ten to a hundred may be observed within a few microseconds after the formation of the radicals, e.g. by a pulsed laser. As the response time of most spectrometers is of the order of 100 μ s, such experiments require modifications of the spectrometer.

An understanding of the CIDNP and CIDEP phenomena was initiated in 1969 [4-5] by the appearance of the basic ideas of what is now known as the Radical Pair Mechanism (RPM). This mechanism predicts correctly the qualitative features of most CIDNP spectra. However, there are many CIDEP spectra which cannot be explained by the RPM. The remaining CIDEP spectra could be accounted for by the Triplet Mechanism (TM) put forward in 1973 [6]. It now appears that all CIDEP spectra may, at least qualitatively be explained by a combination of these two mechanisms.

The radical pair mechanism (RPM) assumes the existence of a pair of transient radicals in the reaction path. These radicals may be directly observed by ESR in favourable cases. On the other hand, in NMR it is the diamagnetic products of the reaction that are observed and all information about the radical pair intermediates is obtained indirectly by the changes these cause on the NMR signal of the products. These changes are rather large, cf. Fig. 1. It is fortunate that many spectra can be qualitatively interpreted by application of simple rules and CIDNP can thus be a useful tool for studying reaction pathways. Valuable quantitative information can also be obtained from CIDNP by application of a quantitative theory, e.g. rate constants, reaction yields, magnetic parameters, and to some extent liquid dynamics.

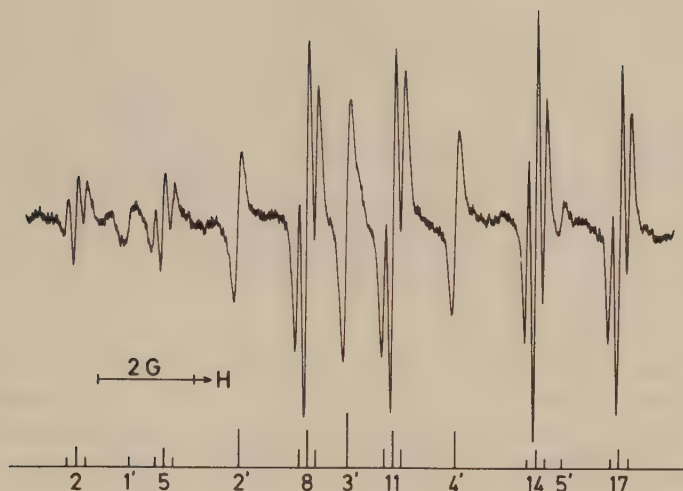


Fig. 2. First derivative ESR spectrum of a steady state system containing two transient radicals. The CIDEP effect is manifested by a reduced intensity of the low field lines and an enhanced intensity of the high field lines. The stick diagram indicates for each species the relative intensities for thermal equilibrium. The five lines from one of the radicals are indicated by primes. From [VIII].

1.1 Radical pair mechanism of CIDNP.

According to the RPM the CIDNP effect is due to a nuclear spin dependent recombination probability, i.e. the probability that two radicals react (recombine) depends on the nuclear spin states of the two radicals. That this assumption may explain the observed spectra can be seen by inspection of Fig. 3. In Fig. 3 the transition frequency of the allowed NMR transitions decreases with increasing transition number and therefore, in a constant frequency variable magnetic field experiment, the transition 1 appears at the lowest field, etc. It is seen that transitions 1 and 3 will be in emission (E) and 2 and 4 will be in absorption (A). The NMR spectrum of the newly formed product is also displayed in Fig. 3 and is identical with Fig. 1A.

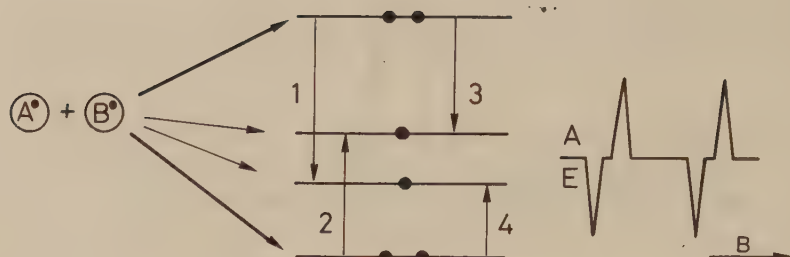


Fig. 3. CIDNP as a result of nuclear spin dependent reaction probabilities. In the middle are the nuclear spin energy levels of a product formed by recombination of the radicals $A^\bullet$ and $B^\bullet$. The initial population of a level (indicated by the number of dots) equals the probability of product formation in the level. Vertical arrows indicate allowed NMR transitions numbered 1 to 4 with decreasing transition frequency. The NMR-spectrum of the newly formed recombination product is shown at the right.

At first sight it seems odd to assume that the probability of recombination should depend on the nuclear spin state, given the fact that the nuclear spin energies are almost negligible compared to the binding energy. However, this follows directly from the two basic assumptions of the RPM for CIDNP and both of them can be intuitively understood. The basic assumptions are: (1) that a chemical reaction of two radicals (recombination) is electron spin selective, i.e. the recombination of the radicals takes place predominantly from one of the total electron spin states, (2) that there exists a nuclear spin dependent interaction within the radicals that causes a mixing of the reactive and unreactive electron spin states. The physical basis for these assumptions is discussed below.

First the electron spin selectivity of a recombination reaction of two radicals forming coupling or disproportionation product is discussed. Since radicals are doublet species (i.e. have electron spin one half) the total electron spin of the pair equals zero (singlet state, S) or one (triplet state, T). When

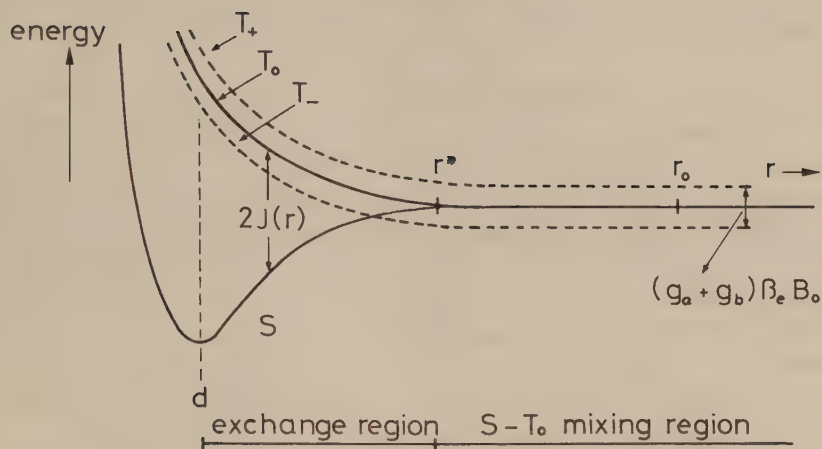


Fig. 4. Relative energies of the singlet and the high field triplet states as a function of the distance between the radicals.

the two radicals are far apart the singlet and triplet states are degenerate, but for small relative distances the singlet and triplet states are split by the exchange interaction as exemplified in Fig. 4.

Due to Brownian motion, the relative separation of the two radicals becomes time dependent. If one assumes that the total spin state of the system is not altered during the time in which the two radicals are in contact (i.e. $r < r^*$ in Fig. 4) then the system "will follow the energy curves", i.e. the energy of the system is given by the stationary energy for any distance. Systems in a triplet state will thus experience a repulsive force for all short distances ($r < r^*$), and the triplet state is anti-bonding. On the other hand, two radicals in a singlet state will experience an attractive force for distances down to $r = d$ where a strong repulsive force sets in. If the depth of the potential well at $r = d$ is larger than kT then the radicals become trapped in the well and thus they have reacted. In the following it is assumed that only singlet pairs can react, which is by far the most common case, but it is worth emphasizing that there do

exist systems which react predominantly from a triplet state. Alterations due to triplet reaction are straight forward.

Mixing of the singlet and triplet states may be caused by differences in Zeeman and/or hyperfine interactions between the radicals. One way of visualizing this is as follows: when the electron spins of the radicals experience different local magnetic fields (by virtue of unequal g-values or hyperfine interactions) they precess at different rates and about different directions, and the system will thus oscillate between the different spin states. This picture is the basis of a geometrical presentation known as the vector model. For the purpose of illustration consider a system placed in a high magnetic field (the field of the spectrometer) where the Zeeman interaction is much larger than the hyperfine interactions. The three high field triplet states (T_+ , T_0 , T_-) with magnetic quantum numbers +1, 0, and -1 now have different energies, as indicated in Fig. 4, and only the T_0 -state remains degenerate with the singlet state for $r > r^*$. Since the amount of mixing of two states caused by a time independent perturbation decreases rapidly with the energy separation of the states, it follows that only the S and T_0 states are mixed in high magnetic fields. It also follows that this mixing occurs most effectively for $r > r^*$ where the S and T_0 states are degenerate. Consequently, the development of significant amount of CIDNP requires two steps: first the radicals must separate to allow S- T_0 mixing; secondly they must reencounter in order to let some of the singlet pairs react.

The series of events leading to CIDNP have been summarized in Fig. 5. For a triplet precursor these events are: a triplet radical pair is produced with a small initial separation $r < r^*$, e.g. by an abstraction process of a molecule in an excited triplet state; triplet pairs do not recombine, therefore the radicals separate by diffusion to distances greater than r^* where the singlet-triplet mixing is operative; if the radicals meet again (reencounter) a fraction of the initially triplet pairs has been converted into singlet pairs by the mixing and these may then react.

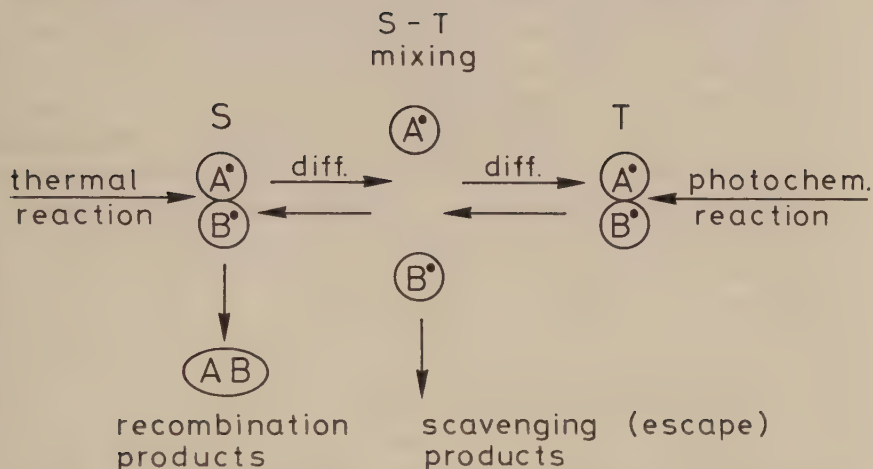


Fig. 5. Schematic representation of the processes involved in the radical pair mechanism of CIDNP. The indicated precursor multiplicity (singlet or triplet) for thermal or photochemical reactions represents the most common case only and is not exclusive.

Since the singlet-triplet mixing may depend on the nuclear spin states of the radicals it follows that the recombination probability may depend on the nuclear spin states of the radicals. Obviously, the $S-T_0$ mixing enhances the recombination probability for initial triplet pairs (e.g. from zero to ϵ). The same argument shows that the recombination probability for initial singlet pairs is reduced by the $S-T_0$ mixing (e.g. from Λ to $\Lambda-\epsilon$). Therefore the NMR spectra of recombination products derived from singlet or triplet precursors have opposite phases (cf. Fig. 3), i.e. lines that appear in emission for one case will appear in absorption for the other case and vice versa.

A radical that does not recombine with its original partner will end up in scavenging products (sometimes called escape products), i.e. the radical reacts with other radicals or become converted to another radical by reaction with a molecule (scavenger) which then reacts with other radicals to

form diamagnetic products. Scavenging products will also show CIDNP and in high magnetic fields the phases of the NMR lines are opposite to those of the recombination product. This is because no spin flip processes are involved in high magnetic fields and thus no net polarization of the sample as a whole is produced. The radical pair mechanism of CIDNP can be considered as a spin sorting mechanism which favours recombination products in some nuclear spin states and scavenging products in the others. No CIDNP is developed if all radicals end up in the same product.

1.2 Radical pair mechanism of CIDEP.

Electron spin polarization (CIDEP) may be developed by the RPM. Contrary to CIDNP, the development of CIDEP does not require the radicals to recombine. It only requires that the radical pair initially has an excess singlet or triplet character and that the exchange interaction between the radicals is non-vanishing. For liquid systems the series of events leading to CIDEP is shown in Fig. 6. Only the high field case is of interest for comparison with experiment. The radical pair has initially an excess singlet or triplet character which is reduced by the S-T₀ mixing when the radicals are apart; upon a reencounter the dephasing of the

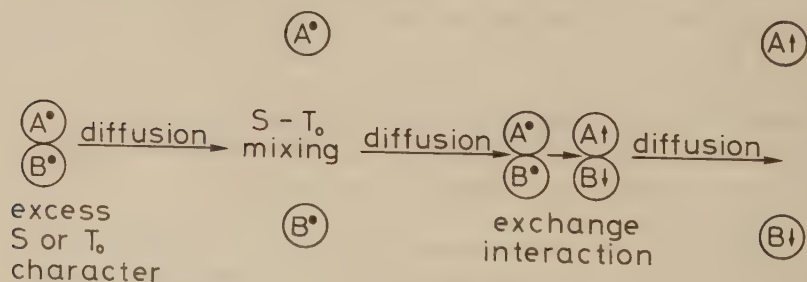


Fig. 6. Schematic representation of the radical pair mechanism for CIDEP. The arrow ↑ indicates that the radical has a net up spin.

electron spins caused by the $S-T_0$ mixing becomes converted to electron spin polarization by a spin sorting mechanism involving the exchange interaction; one radical obtains a net up spin and the other a net down spin of exactly the same magnitude. Thus no net polarization of the sample is developed. Since the $S-T_0$ mixing depends on the nuclear spin state of the radical pair it follows that different hyperfine lines have different electron spin polarization. The actual value of the CIDEP polarization depends on the magnitude as well as on the spatial extent of the exchange interaction. This is contrary to CIDNP, which only depends upon the extent of the exchange interaction (r^* in Fig. 4).

The radical pair mechanism (RPM) may give rise to CIDEP polarization appearing either as initial polarization or as a continuous production of polarization during the lifetime of the radicals. If the radicals are formed with the excess singlet or triplet (T_0) character required for development of CIDEP, then the polarization is developed within 10 ns (cf. Appendix 1) which is shorter than any other process and the polarization thus appears effectively as an initial polarization. Quite often photolytic production of radicals gives triplet radical pairs. Thermal reactions give usually singlet radical pairs. However, CIDEP has never been observed for a thermally driven reaction. On the other hand, CIDEP has been observed in radiolysis where the radicals are produced separately rather than in pairs; the radicals are thus uncorrelated, i.e. the system contains initially equal amounts of singlet and triplet (T_0) characters and consequently no CIDEP can be developed. This situation is changed, however, if the radicals recombine spin selectively whereby singlet pairs disappear and leave a net triplet character; then the CIDEP production can begin and will continue until all radicals have disappeared.

1.3 The triplet mechanism of CIDEP.

Radicals may be "born" with electron spin polarization far

from the equilibrium value. This initial polarization must exist in the precursor since one generally assumes that chemical reactions conserve spin. In the triplet mechanism (TM) the precursor is a molecule in a polarized state. If, for example, the upper Zeeman level of the triplet is populated preferentially (indicated by the dots in Fig. 7, then the radicals produced by the reaction will be polarized as shown schematically in the figure. It is generally believed that the three sublevels of the triplet manifold are equally reactive and consequently no electron spin polarization is produced by the reaction step itself. Of course, the radicals produced by the reaction will only be polarized if the reaction takes place before the triplet polarization is destroyed by triplet spin lattice relaxation. Only electron and hydrogen transfer reactions may be so fast that this condition can be satisfied.

An essential point in the triplet mechanism is the formation of the initial, preferential population of the high field triplet states T_+ , T_0 , and T_- . It is not a trivial matter to see how a tumbling triplet molecule in solution can obtain a preferential population of the high field states which are quantized in the laboratory system. It suffices here to emphasize that the triplet state is populated by intersystem crossing from an excited singlet state produced by light irradiation and that this intersystem crossing is anisotropic in the molecular frame.

1.4 Experimental observables.

As already noted, CIDNP and CIDEP are observed by application of magnetic resonance spectroscopy. It is thus essential to know the connection between the NMR and ESR signals and the CIDNP and CIDEP polarizations produced. For steady state systems there is a proportionality between the absorption signal and the steady state polarization. Any non-equilibrium polarization will decay towards the equilibrium value with a

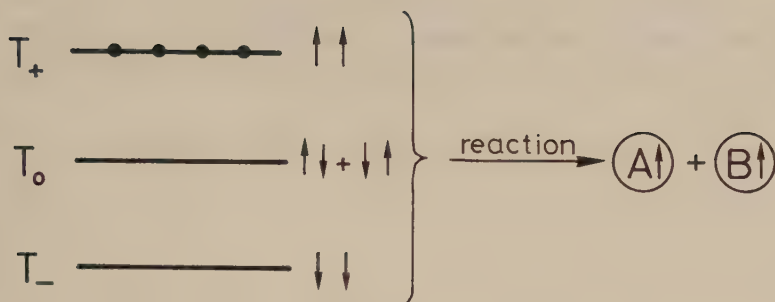


Fig. 7. Oversimplified representation of the triplet mechanism. A preferential population of the high field triplet states T_+ , T_0 and T_- of the precursor molecule is indicated by the dots. Polarization of the radicals follows by conservation of the total spin state under the chemical reaction.

characteristic time constant T_1 during the lifetime of the radical. Thus the steady state polarization depends on the ratio of the life time of the radicals and the spin lattice relaxation time T_1 .

The nuclear spin lattice time is relatively long, of the order of seconds, and then the system is in a quasistationary state, i.e. at any time the NMR-signal is proportional to the instantaneous value of the product of the nuclear spin polarization and the number of molecules. The time dependence of this product can be calculated by simple rate equations.

The electron spin lattice time is of the order of microseconds and in general the ESR-signal is not proportional to the instantaneous value of the product of the electron spin polarization and the number of radicals. This product is proportional to the z-component of the macroscopic magnetization of the sample. Instead the absorption signal is proportional to the y-component in the rotating frame of the magnetization and the dispersion signal is proportional to the x-component. These signals depend on the amplitude of the rf-field, i.e.

on the observing power. A consistent description [XI] of the observable signals can be based on modified Bloch equations generalized to account for radical reactions and polarization productions.

2

ASPECTS OF CIDNP

2.1 Simple rules for CIDNP

An interpretation of NMR-spectra showing CIDNP is facilitated by the use of a set of simple rules. These rules are independent of the diffusional motion of the radicals and were formulated by Kaptein [7] before the appearance of a quantitative theory. The derivation of these rules illustrates the form of the experimental spectra and also indicates how a quantitative theory of CIDNP may be applied to the calculation of observable spectra.

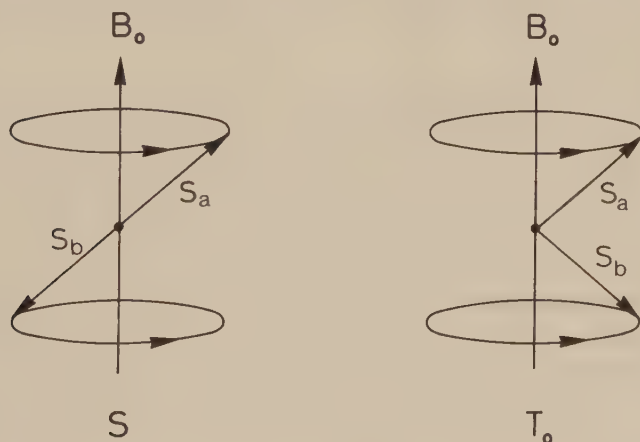


Fig. 8. Vector model representations of the singlet S and the $M=0$ triplet state T_0 . If the precessional rates of $\vec{S}_a$ and $\vec{S}_b$ about the magnetic field B_0 are different, the total spin state will oscillate between S and T_0 .

It is assumed that there is no interaction between two radicals separated by distances greater than r^* (cf. Fig. 4). The electron spins on the two radicals then precess independently of each other about the strong, external magnetic field. If the precessional rates of the two spins are different, the total spin state of the pair will oscillate between the singlet state and the T_0 -triplet state. This is illustrated in Fig. 8, which shows the vector model representations of the S and T_0 states resulting from the vector addition of the individual spins $\vec{S}_a$ and $\vec{S}_b$ of the radicals A and B. The angular frequency of the oscillation between the singlet and triplet states is equal to the difference in Larmor frequencies ($2Q$), i.e.

$$2Q = (g_a - g_b) \beta_e \hbar^{-1} B_0 + \sum_j^a A_j M_j - \sum_k^b A_k M_k. \quad (2.1)$$

The subscripts a and b serve to distinguish quantities belonging to the two radicals and the summations extend over all nuclear spins coupled to the unpaired electron spin. The symbols A_j and M_j denote the isotropic hyperfine constant and the z-component of the nuclear spin j. The external magnetic field is denoted B_0 , g is the isotropic g-factor, and β_e is the Bohr magneton.

The fraction of radical pairs in specified nuclear spin states converted from singlets to triplets or vice versa is proportional to the numerical value of Q if the time available for the mixing is much shorter than the characteristic precession time $1/|2Q|$. Only singlet radical pairs are able to react. Consequently, if all radicals were initially triplets, the fraction of radical pairs recombining in a specified nuclear spin state is proportional to $|Q|$. The population of the different nuclear states of the recombination product is taken to be proportional to $|Q|$ in the following. This implies triplet radical pairs.

Fig. 9 shows the possible populations of the nuclear spin states for a product containing only two nuclei with non-vanishing hyperfine constants and both with spin one half. It is assumed that the two radicals have identical g-factors. The four different nuclear spin states shown to the left of Fig. 9

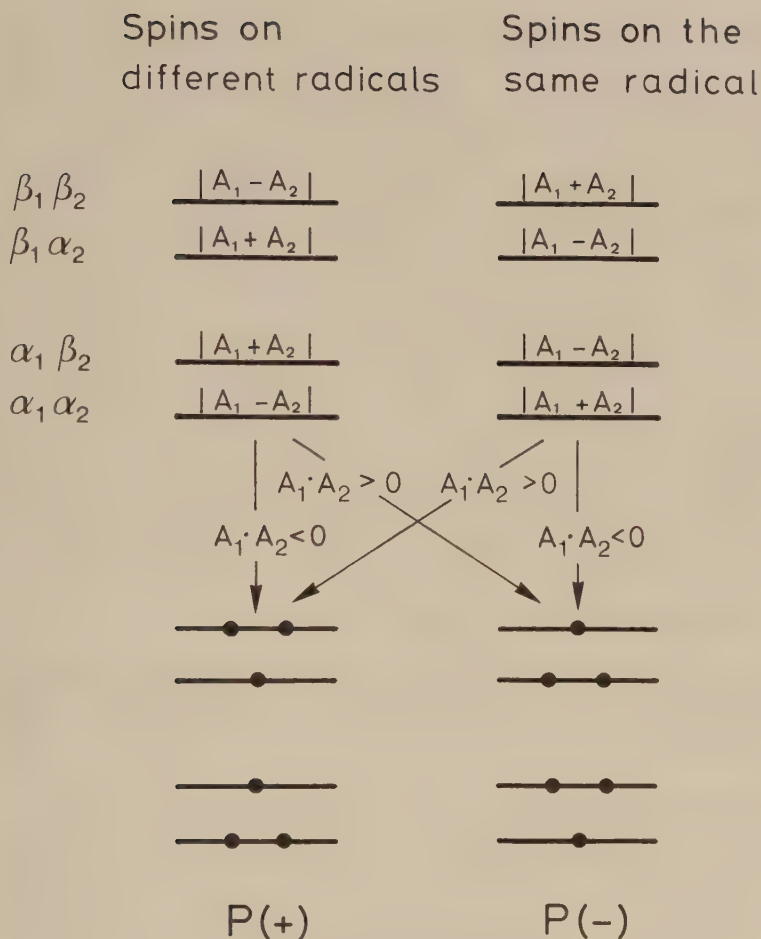


Fig. 9. Populations of the nuclear spin states of a product formed by recombination of two radicals with identical g -factors. The product contains two spin one half nuclei with hyperfine constants A_1 and A_2 . The four different nuclear spin states are shown to the left and are represented by horizontal lines. The populations of the states are proportional to $|Q|$ where Q is defined by Eq.(2.1) and these values are written above each level. The bottom part of the figure shows the two resulting distributions $P(+)$ and $P(-)$. The population of a level is represented by a number of dots. The radical pair was initially in the triplet (T_0) state.

are written as the direct product states of the two spins. The reaction probability and Q depend on these states. The direct product states are the nuclear eigenstates of the radicals but in general they are not eigenstates of the final product (see p. 17). The values of $|Q|$ for the different nuclear spin states depend on the relative signs of the hyperfine constants and on whether the two nuclear spins were originally on the same radical or on different radicals. This follows immediately from Eq. (2.1) and its physical interpretation as the difference in Larmor frequencies between the two radicals. With the aid of Fig. 9 it is concluded that there are only two possible population distributions $P(+)$ and $P(-)$ of the direct product states and that these are the "inverse" distributions of each other. This is also true for scavenging (escape) products which show the opposite population pattern of recombination product, as noted earlier. These results can be combined in the sign relation

$$\text{Product population} = P(\mu A_1 A_2 \sigma_{12} \epsilon) \quad (2.2)$$

where only the sign of the argument matters and $P(+)$ and $P(-)$ are defined in Fig. 9. The signs of the parameters σ_{12} , ϵ , and μ are defined by

$$\begin{aligned} \sigma_{12} &= \begin{array}{l} + \text{ when the nuclei are on the same radical} \\ - \text{ when the nuclei are on different radicals} \end{array} \end{aligned} \quad (2.3)$$

$$\begin{aligned} \epsilon &= \begin{array}{l} + \text{ for recombination product} \\ - \text{ for scavenging (escape) product} \end{array} \end{aligned} \quad (2.4)$$

$$\begin{aligned} \mu &= \begin{array}{l} + \text{ for a triplet precursor and random pairs} \\ - \text{ for a singlet precursor} \end{array} \end{aligned} \quad (2.5)$$

The effect of precursor multiplicity on the population of recombination products as well as the population of scavenging (escape) products were discussed in Sect. 1.1 and the factors μ and ϵ in Eq. (2.2) follow from that discussion (see p.7).

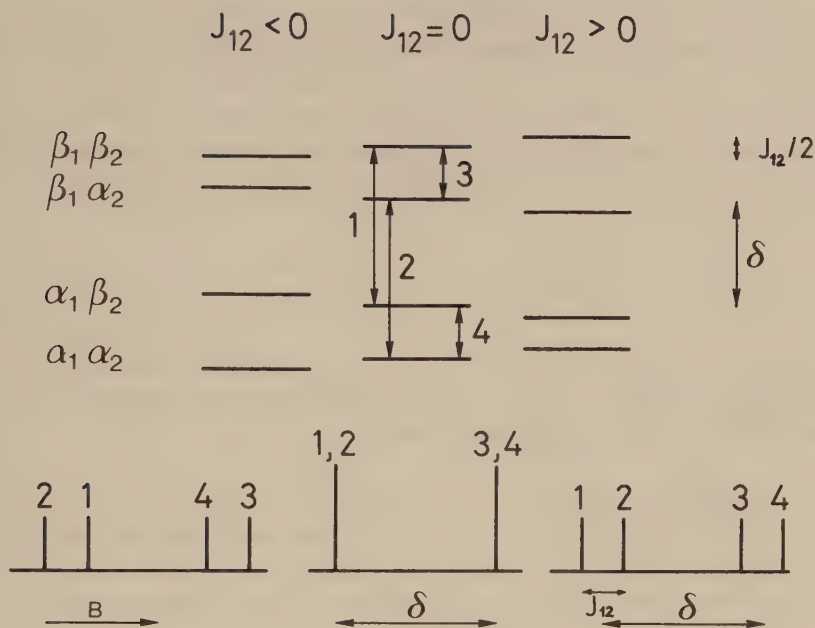


Fig. 10. Energies and NMR spectra of an AX system for different values and signs of the spin-spin coupling constant J_{12} . (The Hamiltonian is given by $H = -\nu_0(1-\sigma_1)I_{1z} - \nu_0(1-\sigma_2)I_{2z} + J_{12}\vec{I}_1 \cdot \vec{I}_2$ with $\delta = \nu_0(\sigma_1 - \sigma_2)$ and $|J_{12}| \ll |\delta|$).

In order to be able to predict the CIDNP-spectrum for the system in Fig. 9 it is necessary to consider the normal NMR spectrum of the product. In the product, the energy eigenstates depend on the strength of the spin-spin interaction $J_{12}\vec{I}_1 \cdot \vec{I}_2$. Only an AX system will be considered, i.e. the spin-spin coupling constant J_{12} is much smaller than the relative chemical shift δ (in s^{-1}). Figure 10 displays the dependence of the energy eigenvalues as a function of the sign and magnitude of J_{12} . The NMR-transitions, numbered 1 to 4, are single spin flip transitions as indicated. The NMR spectra are shown at the bottom of the figure; when $J_{12} = 0$ the spectrum consists of two degenerate lines with spacing δ ; for $J_{12} \neq 0$, the degeneracy is lifted and a multiplet with spacing J_{12} appears. It is important to note that the order of the lines corresponding to specific transitions (e.g. 1 and 2) depends upon the sign of the spin-spin coupling constant J_{12} .

The CIDNP-spectrum of an AX system is constructed in Fig. 11. There are only two types of spectra called E/A or A/E according to the phase of the absorption/emission pattern of each multiplet. This effect of having both emission and absorption lines within the same multiplet is called multiplet effect. The phase of the multiplet effect can be determined by the simple sign rule [7]:

$$\Gamma_{m.e.} = \mu \epsilon A_1 A_2 \sigma_{12} J_{12} \quad \begin{array}{l} + : E/A \\ - : A/E \end{array} \quad (2.6)$$

which follows from Figures 9 and 10. It is worth emphasizing that a multiplet effect is observed when the two radicals have identical or very similar g-factors.

Net effect means that all lines of a multiplet have the same "sign" (A or E). This effect is observed when the radicals have very different g-factors; more precisely when the difference in electronic Zeeman energy is much larger than the hyperfine energies. The effect may be understood with the aid of Fig. 12 which shows the energy levels of a two-spin- $\frac{1}{2}$ -system. The population of the levels by the RPM is again taken to be proportional to the numerical value of Q and this value is written for all levels using an obvious shorthand notation. Also shown in Fig. 12 is the population difference Γ_j for the levels between which the NMR transition j takes place; remember that the line intensity is proportional to Γ_j . The sign convention of Γ is such that positive corresponds to absorption. It follows from Fig. 12 that all members of a multiplet have the same sign of Γ and thus all will be in emission (or all in absorption). The sign of the spin-spin coupling constant has thus no effect on the spectrum, cf. Fig. 10, and the sign of the signal (A or E) is seen to be determined by the simple sign rule

$$\Gamma_{n.e} = \mu \epsilon \Delta g_i A_i \quad \begin{array}{l} + : A \\ - : E \end{array} \quad (2.7)$$

where i indicates the nuclear spin corresponding to the transition. The radical on which i is located is called 1, i.e.

$$\Delta g_1 = g_1(i) - g_2. \quad (2.8)$$

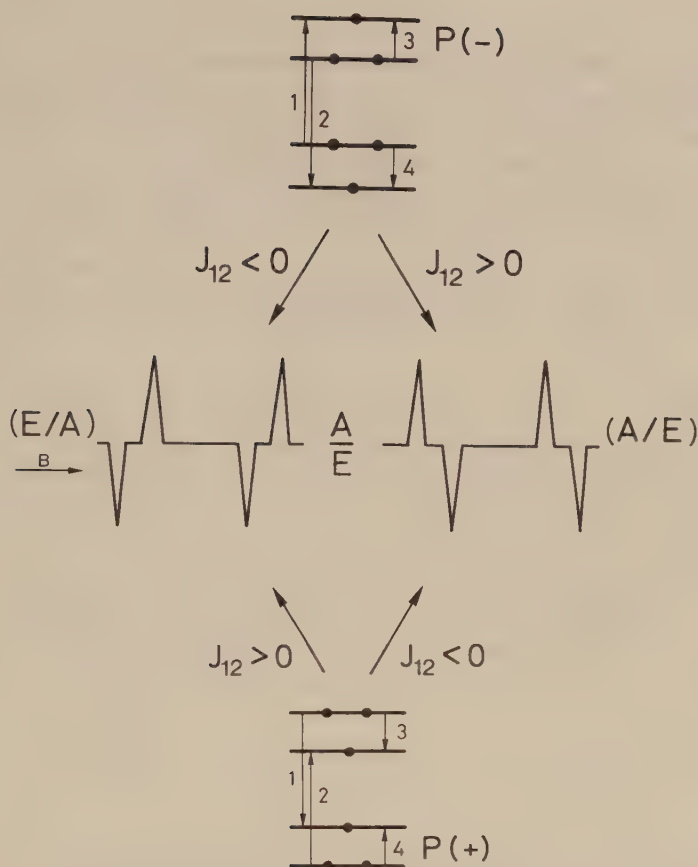
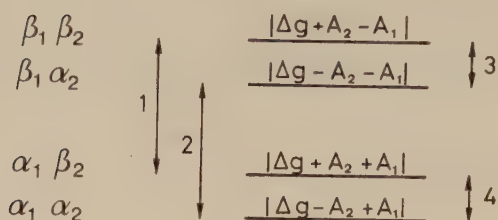


Fig. 11. CIDNP spectra of an AX system. The two possible population distributions $P(+)$ and $P(-)$ were found in Fig. 9. The allowed NMR transitions numbered 1 to 4 are indicated by vertical arrows as in Fig. 10. The directions of the arrows are from high to low level population. The line intensity of a NMR transition is proportional to the population difference of the levels (lower minus upper) between which the transition takes place. A positive(negative) population difference is indicated by an arrow pointing upwards (downwards) and corresponds to absorption (emission). The resulting spectra shown in the middle of the figure are derived with the aid of Fig. 10. Figure 10 determines the relative positions of the lines corresponding to the specific transitions as a function of the sign of the spin-spin coupling constant J_{12} . The two spectral forms are called (E/A) or (A/E) according to the absorption/emission pattern of the multiplet seen from the low field side.

Spins on different radicals



$$\Delta g = (g_1 - g_2) \beta_e \hbar^{-1} B_0$$

$$\Gamma_1 = \Gamma_2 = 2A_1 (g_1 - g_2); \quad \Gamma_3 = \Gamma_4 = -2A_2 (g_1 - g_2)$$

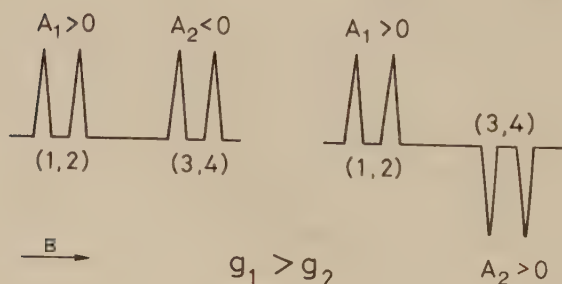


Fig. 12. Populations of the nuclear spin states (cf. Fig. 9) and CIDNP spectra of a product formed by recombination of two radicals with different g -factors g_1 and g_2 . The difference in Zeeman energy indicated by $\Delta g \alpha (g_1 - g_2)$ is assumed to be much larger than the hyperfine constants A_1 and A_2 . The initial electron spin state of the pair is assumed to be T_0 . Thus the population of a nuclear state of the recombination product is proportional to the specific value of $|Q|$ associated with that state. These $|Q|$ values are written above each level. The four NMR transitions are indicated by vertical arrows. The population difference Γ_i is defined as the population of the lower minus the population of the upper of the levels connected by the transition denoted i . The sign of Γ_i determines whether the associated line appears in absorption or emission (+:A and -:E). The indicated sign relations for Γ_i follow from the top figure. The two spectra at the bottom of the figure illustrate the application of the sign relations. Notice that within a multiplet all lines are either in absorption or in emission. This is called net effect.

The pure multiplet effect and the pure net effect shown in Figures 11 and 12 are clearly special cases. Experimental spectra will in general show a combination of multiplet and net effects, which qualitatively can be interpreted by a superposition of the pure cases. Relaxation of the nuclear spins may also change the spectrum. For example, if one of the nuclei has a relaxation time which is much shorter than the other nuclei's, then the corresponding multiplet disappears.

The discussion above showed that a calculation of CIDNP spectra consists of two separate parts: first, a calculation of the populations of the direct product states; second, a transformation of these results into the true eigenstates of the product. The second part is well known as it is involved in any quantitative calculation of NMR spectra. Therefore the following sections are devoted to a discussion of a quantitative theory about populations of the direct product states by radical recombination processes.

2.2 The reencounter picture of translational diffusion.

The idea of visualizing the relative diffusion of two particles as a series of reencounters has proved extremely useful for the development of the theory of CIDNP. The picture was used extensively by Noyes [8] in a treatment of classical reaction kinetics and it was introduced into the CIDNP theory by Adrian [9].

Let d denote the distance of closest approach between two particles and let r_0 be a characteristic distance, of order d , defined such that the particles can be said to be in "contact" in the region $d < r < r_0$. Reaction is allowed in this region of space only. The complete diffusion-reaction process may now be visualized as follows: The particles are initially in contact (first encounter) where they may react with probability λ ; the particles that do not react will separate

by diffusion (i.e. their relative distance becomes greater than r_0); a fraction p of the separated radicals will return to $r=d$ (reencounter) after a diffusive excursion; a fraction λ of these reacts; etc. These reencounter cycles continue until all radicals have reacted or until only a negligible fraction of particles is left to reencounter.

It is convenient to define a collision as the first encounter plus all subsequent reencounters. The probability of reaction per collision Λ is then

$$\begin{aligned}\Lambda &= \lambda + \lambda p(1-\lambda) + \lambda p^2(1-\lambda)^2 + \dots \\ &= \lambda / [1 - p(1-\lambda)]\end{aligned}\quad (2.9)$$

since the fraction λ reacts at the first encounter; of the remaining $(1-\lambda)$ the fraction p reencounters and of these the fraction λ reacts, i.e. $\lambda p(1-\lambda)$ reacts during the first reencounter; etc. Of the three parameters: λ , p , and Λ only the last can be measured. The other parameters are introduced for convenience and should be eliminated at the end of any calculation. However, one may think of relating p to a "contact volume". Suppose the reaction takes place at $r=d$ only and that for some reason the particles need to have a relative separation larger than r_0 before they can be considered separated and can start a reencounter cycle. Then p is simply the probability of reaching d from the initial separation r_0 . For three dimensional continuous diffusion p is given by the expression [10]

$$p(r_0 \rightarrow d) = \frac{df^*(d)}{r_0 f^*(r_0)} \quad (2.10)$$

with

$$1/f^*(r) = r \int_r^{\infty} \exp[U(r)/kT] r^{-2} dr. \quad (2.11)$$

When there is no potential energy $U(r)$ between the particles the dimensionless quantity f^* equals one. Also $f^* < 1$ for repulsive

forces, $f^* > 1$ for attractive forces, and f^* deviates the more from one the larger the range of $U(r)$ is.

2.3 General treatment of CIDNP

Within the RPM only the electron and nuclear spin degrees of freedom are considered and the use of the spin density matrix ρ is convenient for a theoretical description. The equation of motion for ρ may be written as

$$\partial \rho / \partial t = [-iH(r)^{\times} - K(r) - R]\rho(t) \quad (2.12)$$

where the three superoperators between brackets describe spin interactions, chemical reaction (recombination) of the pair, and spin relaxation and/or scavenging of the radicals. The superoperator $H^{\times}$ is defined by its action on any operator A :

$$H^{\times}A = [H, A] \quad (2.13)$$

where $[,]$ is the commutator symbol. The spin Hamiltonian $H(r)$, which must be given in angular units (rad/s), can be written as

$$H(r) = H_A + H_B - J(r) (\frac{1}{2} + 2\vec{S}_A \cdot \vec{S}_B) \quad (2.14)$$

where H_A and H_B are the spin Hamiltonians for the isolated radicals A and B. Usually these are considered the angular averaged of the hyperfine and Zeeman interactions. The last term in Eq. (2.14) represents the exchange interaction between the two radicals and depends parametrically upon their relative distance. $\vec{S}_A$ is the electron spin operator of radical A.

The superoperator $K(r)$ is introduced phenomenologically; the general features of it are that it is non zero only for $r=d$, the distance of closest approach, and that it acts on the electron spin degrees only. Two forms of $K(r)$ have been used. These are:

$$K(r)\rho = \frac{1}{2}k(r)[P_S, \rho]_+ \quad (2.15a)$$

$$K(r)\rho = k(r) P_S \rho P_S \quad (2.15b)$$

when only singlet pairs are allowed to react. In Eq.(2.15a) $[,]_+$ indicates the anticommutator and P_S is the singlet projection operator. The function $k(r)$ is sometimes called the optical potential and can be interpreted as the microscopic rate constant for the relaxation process that leads to a bonding state at the distance r . The differences and similarities between the two forms of $K(r)$, given by Eqs.(2.15), become more evident by considering their matrix representations, using the S-T basis. Note that the matrix representation of a superoperator requires four indices since it operates on operators which require two indices. Both forms of $K(r)$ lead to a diagonal matrix-representation. If Eq.(2.15a) is used for a definition of $K(r)$, then

$$K(r)_{kk} = \begin{cases} k(r) & \text{for } k=SS \\ k(r)/2 & \text{for } k=ST_i \text{ and } T_i S \text{ } (T_i=T_0, T_+, T_-) \\ 0 & \text{otherwise} \end{cases} \quad (2.16a)$$

while Eq.(2.15b) yields

$$K(r)_{kk} = \begin{cases} k(r) & \text{for } k=SS \\ 0 & \text{otherwise} \end{cases} \quad (2.16b)$$

It is seen that both forms of $K(r)$ have the same effect on the singlet diagonal elements, but one of the forms (2.16a) has an effect on the off-diagonal elements ρ_{ST_i} , too. Without going further into a discussion of these two forms of $K(r)$ let us simply note that their difference is unimportant for CIDNP (cf. sect. 2.4).

The last term in Eq.(2.12), i.e. R , represents spin relaxation and for example a Redfield description [11] can be used. This term can also include scavenging of the radicals by simply letting R equal k_S (the pseudo first order rate

constant for scavenging) multiplied by the identity operator.

Complications in solving Eq.(2.12) arise from the time dependence of r , which is caused by the diffusion of the radicals. However, the r -dependence of the Hamiltonian is due to the exchange interaction and this is non-negligible only for $r < r^*$; the characteristic exchange distance r^* , cf. Fig. 4, may be defined by

$$J(r^*) = 10^8 \text{ rad/s} \quad (2.16)$$

where the numerical value is typical for a hyperfine interaction. Since $J(r)$ decays very fast this definition of r^* is rather insensitive to the value at the right hand side.

The reencounter picture is now introduced and the term average is referring to the stochastic description of the relative motion of the two radicals. The average density matrices just before and just after the n 'th reencounter are designated by $\rho(n)$ and $\rho(n)'$, respectively. Since Eq.(2.12) is a linear differential equation the following relations can be obtained:

$$\rho(n)' = \bar{\bar{M}}_1 \rho(n) \quad (2.17)$$

$$\rho(n) = \bar{\bar{M}}_0 \rho(n-1)' \quad (2.18)$$

where the matrices $\bar{\bar{M}}_1$ and $\bar{\bar{M}}_0$ are the time dependent part of the solutions to Eq.(2.12) averaged over the time spent respectively in and outside the exchange region. Since the change of the density matrix at the n 'th reencounter is

$$\rho(n)' - \rho(n) = (\bar{\bar{M}}_1 - \bar{\bar{I}}) \rho(n) \quad (2.19)$$

it follows that the fraction of radical pairs $F(n)$ that reacts during the n 'th reencounter is

$$F(n) = \text{Tr}[(\bar{\bar{I}} - \bar{\bar{M}}_1) \rho(n)]. \quad (2.20)$$

The total fraction of radical pairs reacted (recombined in a collision) is obtained by summing Eq.(2.11) over all reencounters and utilizing Eqs.(2.17) and (2.18):

$$F = \text{Tr} \left[\sum_{n=0}^{\infty} (\bar{I} - \bar{M}_1) (\bar{M}_0 \bar{M}_1)^n \rho(0) \right]. \quad (2.21)$$

This series may be summed to

$$F = \text{Tr} \left[(\bar{I} - \bar{M}_1) [\bar{I} - \bar{M}_0 \bar{M}_1]^{-1} \rho(0) \right]. \quad (2.22)$$

Equation (2.22) is independent of the specific diffusion model and of the exact form of the superoperators appearing in Eq.(2.12). The M-matrices will be evaluated for specific models in the following sections.

2.4 The excluded volume approximation

A calculation of the average quantity $\bar{M}_1$ is difficult for a general situation. Fortunately, the important part of a calculation of F is the $\bar{M}_0$ -determination and the summation given by Eq.(2.21). The simplest approximation for $\bar{M}_1$ is the "excluded volume approximation" which neglects all superoperators in Eq.(2.12) except K(r). The basis for this approximation is that the exchange interaction is the dominant term in the exchange region and the terms H_A , H_B and R may then be neglected. Furthermore, the exchange interaction leaves the diagonal elements of ρ unchanged and these are the elements we are interested in. The only effect of the exchange interaction is thus that it determines the size of the exchange region in which singlet-triplet mixing is suppressed. This effect is important except for small magnetic interactions and low viscosity solvents.

Since K(r) given by Eqs.(2.15) is diagonal in a singlet-triplet representation, the matrix $\bar{M}_1$ can be obtained as the matrix representation of K(r) with k(r) replaced by $1-\lambda$ where as before λ is the probability of reaction per encounter. It is

now useful to define a matrix $\bar{\lambda}$ as

$$-\bar{\lambda} = \bar{M}_i - \bar{I} \quad (2.23)$$

and another diagonal matrix $\bar{\Lambda}$ in the S-T representation as

$$\Lambda_{kk} = \lambda_{kk} / [1 - p(1 - \lambda_{kk})]. \quad (2.24)$$

Clearly $\bar{\Lambda}$ is nothing but the matrix representation of $K(r)$ with $k(r)$ replaced by $1 - \Lambda$; recall that Λ is the probability of reaction per collision and thus a measurable quantity. After a few algebraic manipulations Eq.(2.22) can be rewritten to

$$F = \text{Tr}\{\bar{\Lambda} [\bar{I} + (1-p)^{-1} (p\bar{I} - \bar{M}_0) (\bar{I} - \bar{\Lambda})]^{-1} \rho(0)\} \quad (2.25)$$

This expression is convenient for expansions since $p\bar{I} - \bar{M}_0$ is small, for small magnetic interaction and low viscosity (see the following section). The first order term is

$$F \approx \text{Tr}\{\bar{\Lambda} [\bar{I} - (1-p)^{-1} (p\bar{I} - \bar{M}_0) (\bar{I} - \bar{\Lambda})] \rho(0)\}. \quad (2.26)$$

For pure singlets initially ($\rho(0) = |S\rangle\langle S|$), Eq.(2.26) can be written explicitly as

$$F(S) = \Lambda - \Lambda (1-\Lambda) [p - (M_0)_{SS,SS}] / (1-p) \quad (2.27)$$

and for a pure triplet state T_i initially

$$F(T_i) = \Lambda(M_0)_{SS, T_i T_i} / (1-p). \quad (2.28)$$

It is interesting to note that Eqs.(2.27) and (2.28) are obtained irrespective of the form of $K(r)$ used, Eqs.(2.16a) or (2.16b). It is also interesting that to this order of approximation the effect of including all reencounters is simply to replace λ by Λ in the single reencounter result and then to divide by $(1-p)$.

All results for mixed initial conditions are obtained by superposition of the above results.

It follows from Eqs.(2.27) and (2.28) that the largest CIDNP effect is obtained when $\Lambda=\frac{1}{2}$ for a singlet precursor and when $\Lambda=1$ for a triplet precursor, i.e. for highly reactive radicals.

2.5 Evaluation of the average matrix, $\bar{\bar{M}}_O$

The matrix representation of the superoperator

$$S_O = H_A^x + H_B^x + iR \quad (2.29)$$

is a complex, symmetric matrix which can be diagonalized by the transformation

$$\bar{U}_O^{-1} \bar{\bar{S}}_O \bar{U}_O = \bar{\bar{D}}_O \quad (2.30)$$

where $\bar{U}_O$ is the matrix of right eigenvectors of $\bar{\bar{S}}_O$ and $U_{ij}^{-1} = U_{ji}$. The eigenvalues d_k of $\bar{\bar{S}}_O$ are in general complex and form the diagonal matrix $\bar{\bar{D}}_O$.

The matrix $\bar{\bar{M}}_O$ introduced in Eq.(2.18) can now be written as

$$\bar{\bar{M}}_O = \bar{U}_O < \exp(-i\bar{\bar{D}}_O t) >_t \bar{U}_O^{-1} \quad (2.31)$$

where $< >_t$ indicates an average over the time spent outside the exchange region in a single reencounter cycle. It is computationally much more convenient to calculate an average over the first arrival time at $r=d$ starting from r_O . Note, however, that this approach allows S-T mixing in the region $d < r < r_O$ when the radicals are approaching but not when they are leaving. Physically there is no S-T mixing in the exchange region $d < r < r^*$. Therefore the model parameter r_O must be chosen larger than r^* and the choice

$$r_O - d = 2(r^* - d) \quad (2.32)$$

is physically reasonable and gives excellent agreement with the accurate numerical results of [IV].

A calculation of $\bar{M}_0$ by Eq.(2.31) consists of two parts: first, a solution of the eigenvalue problem for $\bar{S}_0$. Second, a calculation of the average quantity

$$\langle \exp(-id_k t) \rangle_t = \int_0^\infty \exp(-id_k t) f(t, d|r_0) dt \quad (2.33)$$

where $f(t, d|r_0)$ is the probability density of first arrival at $r=d$ at time t for an initial separation $r_0 > d$. The probability of a reencounter p , introduced in Eq.(2.9), is related to $f(t, d|r_0)$ by the relation

$$p = \langle 1 \rangle_t = \int_0^\infty f(t, d|r_0) dt. \quad (2.34)$$

If $f(t)$ decays to zero within a time t_0 , and $|d_k|t_0 \ll 1$ then $\langle \exp(-d_k t) \rangle_t \approx p$. Consequently, $\bar{M}_0 \approx p\bar{I}$ when the diffusion is fast (low viscosity of the solvent) and the magnetic interaction is small. It is then convenient to use $(p\bar{I} - \bar{M}_0)$ as the expansion parameter, as already done in obtaining Eq.(2.26).

For the continuous free diffusion model analytic expressions for both $f(t)$ [10] and the average value in Eq.(2.33) can be derived [IX]. The latter is

$$\langle \exp[-i(a-ib)t] \rangle_t = p \exp(-z_+) \exp(-iz_-) \quad (2.35)$$

where z_+ and z_- are defined as

$$z_\pm = \frac{1-p}{p} \left(\frac{d^2}{2D} \right)^{\frac{1}{2}} [(b^2 + a^2)^{\frac{1}{2}} \pm b]^{\frac{1}{2}}, \quad (2.36)$$

p is given by Eq.(2.10) with $f^*=1$, and D is the diffusion constant.

For other diffusion models, e.g. diffusion in a potential field, the average value in Eq.(2.33) has not been given in analytic form. It can be calculated numerically by the finite difference method discussed in Sect. 3.2 and it can be calculated approximately by a perturbation technique [12].

2.6 High field CIDNP. Analytic and numerical results.

The spin Hamiltonian H_A for an isolated radical is assumed to consist of the isotropic parts of the Zeeman and hyperfine interactions. In high magnetic fields only the secular terms, i.e. terms containing the operators S_z and I_z , have to be included. The total Hamiltonian for the pair of radicals A and B can then conveniently be written as⁺

$$H(r) = H^O(r) + H' \quad (2.37)$$

where $H^O(r)$ and H' are given by

$$H^O(r) = \frac{1}{2}(g_a + g_b)\beta_e \hbar^{-1} B_O (S_{az} + S_{bz}) + \frac{1}{2} \left[\sum_j A_{aj} I_{jz} + \sum_k A_{bk} I_{kz} \right] \times (S_{az} + S_{bz}) - J(r) \left(\frac{1}{2} + 2\vec{S}_a \cdot \vec{S}_b \right) \quad (2.38a)$$

$$H' = \frac{1}{2}(g_a - g_b)\beta_e \hbar^{-1} B_O (S_{az} - S_{bz}) + \frac{1}{2} \left[\sum_j A_{aj} I_{jz} - \sum_k A_{bk} I_{kz} \right] \times (S_{az} - S_{bz}). \quad (2.38b)$$

Subscript a and b serve to distinguish quantities belonging to the two radicals and the summations extend over all nuclear spins coupled to the unpaired electron spin. Both terms are clearly diagonal in a nuclear spin basis equal to the direct product of all the nuclear spin eigenstates of $\vec{I}_k^2$ and I_{kz} (k denotes the nucleus). In this basis an effective electron spin Hamiltonian equal to the sum of

$$H^O(r) = E(S_{az} + S_{bz}) - J(r) \left(\frac{1}{2} + 2\vec{S}_a \cdot \vec{S}_b \right) \quad (2.39a)$$

and

$$H' = Q(S_{az} - S_{bz}) \quad (2.39b)$$

is obtained. The parameters E and Q depend on the total nuclear spin state of the two radicals

⁺using the identity: $aA + bB = \frac{1}{2}(a+b)(A+B) + \frac{1}{2}(a-b)(A-B)$

$$\frac{E}{Q} = \frac{1}{2}(g_a + g_b) \beta_e \hbar^{-1} B_0 + \frac{1}{2} \left(\sum_j A_j^a M_j + \sum_k A_k^b M_k \right) \quad (2.40)$$

The parameters E and Q are half the sum and difference of the Larmor frequencies of the individual radicals. The definition of Q by Eq.(2.40) is identical with Eq.(2.1). In the coupled basis (S-T) of the electron spins, the matrix representation of $H^0(r)$ is diagonal and H' is purely off-diagonal. This follows, for example, by noting that $H^0(r)$ commutes with S_a^2 , S_b^2 , S^2 , and S_z (where $S = S_a + S_b$ is the total electron spin) while H' only commutes with S_a^2 , S_b^2 , and S_z . The selection rules for H' are thus $\Delta S = \pm 1$ and $\Delta M = 0$ and consequently only the singlet state and the T_0 state are mixed by H' . The T_+ and T_- states can thus be left out of the calculation, unless spin relaxation is included explicitly.

The matrix representation of $H(r)^{\times}$ is

$$H(r)^{\times} = \begin{bmatrix} SS & ST_0 & T_0 S & T_0 T_0 \\ 0 & -Q & +Q & 0 \\ -Q & 2J(r) & 0 & +Q \\ +Q & 0 & -2J(r) & -Q \\ 0 & +Q & -Q & 0 \end{bmatrix} \quad (2.41)$$

The solution to the rate equation for $\rho(t)$ Eq.(2.12) can be obtained in closed form [IX] when the distance r is kept fixed and reaction and relaxation are neglected. Since this solution will be used in the following sections on CIDEP it is given explicitly:

$$\begin{bmatrix} \rho_{ST_0} - \rho_{T_0 S} \\ \rho_{ST_0} + \rho_{T_0 S} \\ \rho_{SS} - \rho_{T_0 T_0} \end{bmatrix} (t) = \begin{bmatrix} c(t) & -i \frac{J}{\omega} s(t) & i \frac{Q}{\omega} s(t) \\ -i \frac{J}{\omega} s(t) & \frac{Q^2}{\omega^2} + \frac{J^2}{\omega^2} c(t) & \frac{QJ}{\omega^2} (1-c(t)) \\ i \frac{Q}{\omega} s(t) & \frac{QJ}{\omega^2} (1-c(t)) & \frac{J^2}{\omega^2} + \frac{Q^2}{\omega^2} c(t) \end{bmatrix} \bar{\rho}(0) \quad (2.42a)$$

and

$$(\rho_{SS} + \rho_{T_O T_O})(t) = (\rho_{SS} + \rho_{T_O T_O})(0) \quad (2.42b)$$

where ω , $s(t)$ and $c(t)$ are defined as

$$\omega = (Q^2 + J^2)^{\frac{1}{2}} \quad (2.42c)$$

$$s(t) = \sin(2\omega t)$$

$$c(t) = \cos(2\omega t). \quad (2.42d)$$

The M_O -matrix needed in Eq.(2.25) for a calculation of the fundamental CIDNP quantity F is obtained by setting $J(r)=0$ in Eq.(2.42a) and then averaging the resulting matrix over time by use of the probability density $f(t, d|r_O)$ for the first arrival time at d , starting from r_O .

The probability of reaction F may be calculated by Eq.(2.25). The matrix inversion in Eq.(2.25) can be performed analytically and the following general relations expressing F in terms of just two parameters Λ and F^* are obtained:

$$F(T_O) = \Lambda F^* / [1 + F^* (1 - \Lambda)] \quad (2.43a)$$

$$F(S) - \Lambda = -\Lambda (1 - \Lambda) F^* / [1 + F^* (1 - \Lambda)] \quad (2.43b)$$

$$F(R.I.) - \frac{\Lambda}{2} = \frac{1}{2} \Lambda^2 F^* / [1 + F^* (1 - \Lambda)]. \quad (2.43c)$$

In these relations the initial condition is written in parantheses and R.I. stands for random initial which is the initial condition corresponding to a "random" encounter of two radicals derived from different precursor molecules. Some authors prefer to call the R.I. precursor for F precursor, where F stands for free radicals.

The parameter F^* is defined as $F(T_O; \Lambda=1)$, i.e. the probability of forming geminate product from a triplet precursor under the condition that singlet radical pairs react with probability one (at $r=d$). F^* measures the conversion from triplets to singlets, and vice versa, i.e. the efficiency

of the S-T₀ mixing. The following expression for F* is obtained [IX] in the absence of scavenging and relaxation processes

$$F^* = \frac{p(1-c) + p^2[(1-c) - (1-s^2-c^2)]}{2(1-p)^2 + 3p(1-c) - p^2[(1-c) + (1-s^2-c^2)]} \quad (2.44)$$

In the presence of scavengers one finds [IX] that the fundamental relations (2.43) again apply and that F* is given by

$$F^* = \frac{p(c_0-c) + p^2[(c_0-c)c_0 - (c_0^2 - c^2 - s^2)]}{2(1-pc_0)^2 + 3p(c_0-c) - p^2[(c_0-c)c_0 + (c_0^2 - c^2 - s^2)]} \quad (2.45)$$

The parameters c, s, and c₀ are defined as

$$c = \langle \cos(2Qt) \exp(-kt) \rangle_t / p \quad (2.46a)$$

$$s = \langle \sin(2Qt) \exp(-kt) \rangle_t / p \quad (2.46b)$$

$$c_0 = c(Q=0) \quad (2.46c)$$

where k is the pseudo-first order rate constant for a scavenging reaction. Alternatively k is equal to k_s(S) where (S) is the concentration of scavengers and k_s is the second order rate constant for the scavenging process.

The relations (2.43) which express F in terms of the parameters Λ and F* are valid for all classical diffusion models. They give the excess probability of forming recombination product due to S-T₀ mixing and this is the quantity of interest for calculation of CIDNP spectra. Similarly the expressions (2.44) and (2.45) for the singlet-triplet mixing parameter F* are valid for all diffusional models. The assumed diffusion model enters the calculation through a calculation of the quantities c, s, and c₀ only. For three-dimensional, continuous, free diffusion these quantities may be given in closed form, cf. Eq. (2.35)

$$c = \exp(-z_+) \cos(z_-) \quad (2.47a)$$

$$s = \exp(-z_+) \sin(z_-) \quad (2.47b)$$

where the parameters z_+ and z_- are defined as

$$z_{\pm} = \frac{1-p}{p} \left(\frac{d^2}{2D} \right)^{\frac{1}{2}} [(k^2 + 4Q^2)^{\frac{1}{2}} \pm k]^{\frac{1}{2}}. \quad (2.47c)$$

The parameters z_+ and z_- are approximated by

$$z = \frac{1-p}{p} \left(\frac{Qd^2}{D} \right)^{\frac{1}{2}} \quad (2.47d)$$

when $k \ll Q$ and this is the no scavenging situation for which Eq.(2.44) is valid. Note that p is related to the extent of the exchange interaction through Eq.(2.32).

Approximate results, which are independent of p , are obtained for $z_+ \ll 1$. Expansion of c, s , and c_0 in powers of z_+, z_- , and z_0 , substitution in Eq.(2.45), and retaining only first order terms yields

$$F^* \approx \frac{1}{2} (Qd^2/D)^{\frac{1}{2}} \quad (2.48a)$$

for $k \ll Q$ (i.e. for negligible scavenging), and

$$F^* \approx \frac{1}{4} (kd^2/D)^{\frac{1}{2}} Q^2/k^2. \quad (2.48b)$$

for $Q \ll k$ (i.e. for fast scavenging).

The square root dependence of F^* on Q in Eq.(2.48a) is characteristic of three-dimensional free diffusion and is obtained as well by approaches [9] that include a single reencounter only. The independence of p is a result of the inclusion of all reencounters. Equation (2.48b) shows that a scavenging reaction may "enhance" the nuclear spin state dependence of F^* from a square root to a quadratic dependence. Note, however, that an enhanced Q -dependence is accompanied by a reduction of F^* by a factor up to $\frac{1}{2} (Q/k)^{3/2}$.

The condition for the validity of the simplifying equations (2.48) is that $z_+ \ll 1$ and in many cases this cannot be fulfilled. Consider, for example, two identical radicals with nuclear spin $\frac{1}{2}$, an isotropic hyperfine constant equal to 15 Gauss (1.5 mT) and a molecular diameter of 4Å. For a solvent with viscosity $\eta=13$ cP (e.g. ethylene glycol) a value of 0.494 is obtained for $(Qd^2/D)^{\frac{1}{2}}$ while 0.137 is obtained for solvents with a viscosity about 1 cP such as isopropanol, ethanol, and methanol. In the above estimation it was assumed that the single particle diffusion constant D' could be calculated by the Stokes-Einstein relation

$$D' = \frac{kT}{6\pi\eta r} \quad (2.49a)$$

where r is the radius of the sphere. The relative diffusion constant D is the sum of the individual diffusion constant D' .

The Stokes-Einstein relation gives accurate values of D' for solute molecules which are much larger than the solvent molecules. A more general expression for the diffusion constant is supplied by the Gierer and Wirtz theory [13] which writes D' as

$$D' = \frac{kT}{6\pi\eta r f_t} \quad (2.49b)$$

where f_t is called the microfriction factor. This theory accounts satisfactorily for the dependence of the observed diffusion constant on the relative sizes of the solute and solvent molecules, and on the viscosity and temperature of the solvent [13]. Unfortunately the theory does not supply a unique value of f_t for a system with approximately equal sizes of solute and solvent molecules. It is thus of interest to determine f_t by CIDNP. Using the above relations for F^* this may indeed be possible and most convenient for $(Qd^2/D) \ll 1$.

In principle, it should be possible, too, to get an experimental determination of p for systems with "large" values of Qd^2/D . This would then, by Eqs.(2.10) and (2.32), lead to an

experimental determination of the extent of the exchange interaction.

The reactivity parameter Λ is considered an experimental parameter which determines the reaction yield of a radical pair reaction. There is an interesting connection between Λ and D in the expression for the observable macroscopic rate constant for a reaction of two distinguishable R.I. radicals [10]

$$k_{\text{obs}} \approx 4\pi D d f^* \Lambda / 4. \quad (2.50)$$

Accurate numerical results for the singlet-triplet mixing parameter F^* are given in [IV] for a diffusion model that includes electrostatic interaction between the radicals in the Debye-Hückel fashion. Some of the results are displayed in Fig. 13. The limiting form of F^* for small values of Qd^2/D is found to be

$$F^* = \frac{1}{2} (Qd^2/D)^{\frac{1}{2}} f^* \quad (2.51)$$

where f^* is given by Eq.(2.11), i.e. to lowest order the effect of the potential interaction is to replace the distance of closest approach d by the "effective distance of closest approach" df^* .

The results of a numerical calculation of F^* for a diffusion model with a space dependent diffusion coefficient $D(r)$ are presented in [V]. It is found that the limiting form of F^* given by Eq.(2.51) again applies, provided f^* is interpreted as

$$1/f^* = d \int_d^{\infty} \exp \left[\frac{U(r)}{kT} \right] \frac{D(\infty)}{D(r)} \frac{dr}{r^2}. \quad (2.52)$$

This definition of f^* is identical with Eq.(2.11) for a space independent diffusion coefficient.

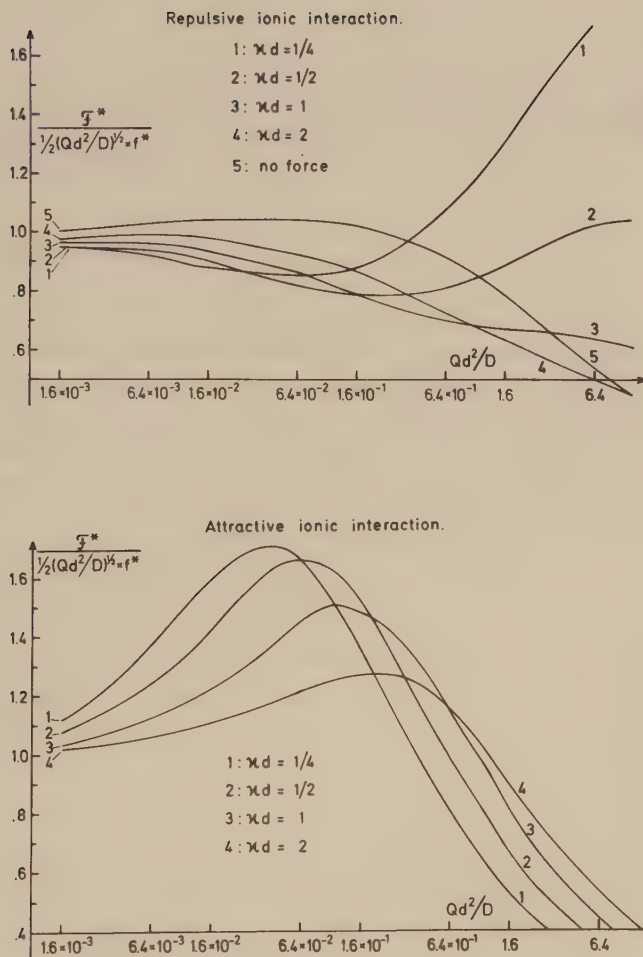


Fig. 13. Numerical results for F^* . The diffusion model includes the effect of electrostatic interaction between the radicals. Debye-Hückel potential $U(r)$ is used to account for charge shielding effects due to the ionic atmosphere. The chosen values of $U(d)=5kT/(1+\kappa d)$ and the indicated values of κd correspond roughly to aqueous solutions with ionic concentrations of 0.01M for $\kappa d = \frac{1}{4}$ to 0.25M for $\kappa d=2$, for double charged radicals with a diameter of 6Å. The numerical method is discussed in Sect. 3.3. From [IV].

3

THE RADICAL PAIR MODEL. CIDEP

3.1 A simple derivation

The electron spin polarization of a radical A is defined as the difference in populations between the two electron spin eigenstates. As ordinarily the experimental situation is that the Zeemann interaction is much larger than the hyperfine interactions these eigenstates are the high field states α (up) and β (down). The electron spin polarization P_a of radical A in nuclear state a can then be written as

$$P_a = \rho(a)_{\beta\beta} - \rho(a)_{\alpha\alpha} = -2\text{Tr}[S_{Az}\rho(a)] \quad (3.1a)$$

where the trace is over the electron spin states of A and $\rho(a)$ is the electron spin density matrix of radical A in nuclear state a, i.e.

$$\rho(a) = \text{Tr}_a[|a\rangle\langle a|\rho(A)] = \langle a|\rho(A)|a\rangle \quad (3.1b)$$

where $\rho(A)$ is the complete spin density matrix of A and the trace is over the nuclear spin states of A. It is convenient to introduce a quantity P_{ab} by the definition

$$P_{ab} = -2\text{Tr}[S_{Az}\rho(a,b)] \quad (3.2a)$$

in which $\rho(a,b)$ is the electron spin density matrix for the pair of radicals A and B in specified nuclear spin states a and b and the trace is over the electron spin states of the pair. The formal definition of $\rho(a,b)$ is

$$\rho(a,b) = \text{Tr}_{a',b'}[|ab\rangle\langle ab|\rho_T] = \langle ab|\rho_T|ab\rangle \quad (3.2b)$$

where ρ_T is the complete spin density matrix for the pair of radicals and the trace is over all nuclear spin states. The electron spin density matrix $\rho(a,b)$ obeys the equation of motion (2.12) with the effective electron spin Hamiltonian (2.39). It is implied that the nuclear spin states are chosen to be eigenstates of the total Hamiltonian, i.e. in high fields they are eigenstates of I_k^2 and I_{kz} for all nuclear spins k .

The quantity P_{ab} may be interpreted as the conditional electron spin polarization of radical A in nuclear spin state a when radical B is known to be in nuclear spin state b . The unconditional polarization P_a of radical A in nuclear state a is obtained by averaging P_{ab} over the nuclear spin states of B

$$P_a = \sum_b P_{ab} / \Sigma 1. \quad (3.2c)$$

The division in Eq.(3.2c) by the number of nuclear spin states of B ($\Sigma 1$) implies that the initial value of $\rho(a,b)$ is normalized to unity with respect to the electron spin states for any set of a and b .

As the conditional polarization P_{ab} depends on Q only, cf. Eq.(2.40), it can be calculated for a general system and is thus the quantity of theoretical interest. On the other hand, the observable unconditional polarization P_a depends on the energies of the nuclear spin states of radical B through Eq.(3.2c).

The sign convention in Eq.(3.1a) yields positive equilibrium polarization

$$P_{eq} = \frac{1}{4} \beta_e g_a B_0 / kT. \quad (3.3)$$

The value of P_{eq} is 0.70×10^{-3} for X-band experiments ($\nu=9500$ Mhz, $B_0 \approx 3300G=0.33T$) at room temperature $T=300K$.

In the following $\rho(a,b)$ is simply denoted ρ as no confusion is likely to occur. This is similar to Section 2.5 and many of the results derived there can be used here. Again the singlet and triplet states are used as a basis for the electron spin space of the pair. Equation (3.2a) for the (conditional) polarization of radical A can be rewritten in a convenient form by application of the identity $2S_{az} = (S_{az} - S_{bz}) + (S_{az} + S_{bz})$

$$P_{ab}(t) = -[\rho_{ST_O}(t) + \rho_{T_O S}(t)] + [\rho_{T_- T_-}(t) - \rho_{T_+ T_+}(t)] \quad (3.4a)$$

Similarly the polarization of radical B is

$$P_{ba}(t) = +[\rho_{ST_O}(t) + \rho_{T_O S}(t)] + [\rho_{T_- T_-}(t) - \rho_{T_+ T_+}(t)] \quad (3.4b)$$

In high magnetic fields the matrix elements $\rho_{T_- T_-}$ and $\rho_{T_+ T_+}$ are time independent, cf. Sect. 2.4, and no RPM polarization can be developed by these terms. Polarization by the RPM can arise from the terms in the first bracket only. Since these terms have opposite signs for the two radicals it follows that no net polarization is developed.

The time dependence of the density matrix is given by Eq. (2.42a) when the distance between the radicals is assumed fixed. The diagonal elements of the initial density matrix may be assumed to be the only non-vanishing elements. It then follows from Eqs. (2.42a) and (3.4a) that polarization is generated according to

$$P_{ab}(t) = -(QJ/\omega^2)(1 - \cos(2\omega t))(\rho_{SS} - \rho_{T_O T_O})(0) \quad (3.5)$$

where $\omega^2 = Q^2 + J^2$. If the radicals separate at time t with a probability density equal to

$$P(t) = \tau^{-1} \exp(-t/\tau) \quad (3.6)$$

then the average polarization generated before separation is

$$P_{ab} = -\frac{4QJ\tau^2}{1 + 4(Q^2 + J^2)\tau^2}(\rho_{SS} - \rho_{T_O T_O})(0) \quad (3.7)$$

The polarization generated by this mechanism is sometimes called cage polarization because it is generated when the radicals are together (in the "solvent cage").

In liquids the cage polarization is negligible compared with the reencounter polarization discussed below. However for photochemical processes in the solid state the cage mechanism may be important and it appears to be responsible for the polarization observed from the primary processes of photosynthesis [16,17].

The reencounter mechanism, usually just called radical pair mechanism, involves two steps as indicated in Fig. 6, i.e. the radicals must separate and reencounter later. When the radicals are separated the exchange interaction is negligible ($J=0$). According to Eq.(2.42a) an off-diagonal element of the density matrix is developed

$$(\rho_{ST_O} - \rho_{T_O S})(t) = i \sin(2Qt) (\rho_{SS} - \rho_{T_O T_O})(0). \quad (3.8a)$$

The average value of this element with respect to the duration of a reencounter can be written as

$$\langle \rho_{ST_O} - \rho_{T_O S} \rangle_t = i \operatorname{sgn}(Q) p_s (\rho_{SS} - \rho_{T_O T_O})(0) \quad (3.8b)$$

where s is defined by Eq.(2.46b) with $k=0$ and p is the reencounter probability. When the radicals reencounter the element in Eq.(3.8b) is converted to electron spin polarization by the exchange interaction. The result of this conversion is obtained by Eq.(2.42a) with the initial condition given by Eq.(3.8). For $|J| \gg |Q|$ the result is:

$$(\rho_{ST_O} + \rho_{T_O S})(t) = \operatorname{sign}(QJ) p_s \sin(2|J|t) (\rho_{SS} - \rho_{T_O T_O})(0). \quad (3.9)$$

If the average time spent in the exchange region is given by the probability density (3.6) then the averaged polarization P_{ab} developed in this single reencounter cycle becomes equal to

$$P_{ab} = -\text{sgn}(QJ) \frac{2|J|\tau_J}{1+(2J\tau_J)^2} p_s(Q) (\rho_{SS}^{-\rho_{T_O T_O}})(0). \quad (3.10)$$

For free diffusion $s(Q)$ is given by Eqs.(2.47),

$$s(Q) = \exp(-z)\sin(z), \quad z = \frac{1-p}{p} \left(\frac{Qd^2}{D}\right)^{\frac{1}{2}} \quad (3.11)$$

For small magnetic interactions, i.e. $z \ll 1$, the characteristic function $s(Q)$ given by Eq.(3.11) is approximated by $s \approx z$. Furthermore, in this limit, but only in this limit, the effect of multiple reencounters can be included simply by dividing the single reencounter result by $(1-p)$, cf. Eqs.(2.27) and (2.28) and the following discussion. Equations (3.11) and (3.12) thus simplify to

$$P_{ab} = -\text{sgn}(QJ) \frac{2|J|\tau_J}{1+(2J\tau_J)^2} \left(\frac{Qd^2}{D}\right)^{\frac{1}{2}} (\rho_{SS}^{-\rho_{T_O T_O}})(0). \quad (3.12)$$

Earlier theoretical works have been confined to the small magnetic interaction region ($z \ll 1$) for which Eq.(3.12) has been derived. The above derivation is similar to that used by Adrian [14] who obtained the square root dependence but neglected to consider the J -dependence and the effect of more than one reencounter. Evans et al. [15] obtained an approximate solution to the stochastic Liouville equation for a special form of $J(r)$: $J(r) = J_0 \delta(r-d)$. Their result for P_{ab} is identical with Eq.(3.12).

The relation (3.12) for the polarization is not supposed to be of quantitative validity. It is valid for $z \ll 1$ only, but the real limitation is connected with the J -dependence. In the derivation it was assumed that the exchange interaction was constant in the exchange region and that the time spent in this region was given by the exponential probability density (3.6). Even accepting these simplifying assumptions the problem of relating the average exchange time τ to physical quantities remains. However, several important conclusions can be drawn from the approximate results. The polarization can be given as a product of a function that depends on Qd^2/D and p (the extent of $J(r)$) and a function that

depends on $J(r)$. For $z \ll 1$ a square root dependence upon Q is obtained for the polarization P_{ab} which furthermore is independent of p . This is similar to high field CIDNP but for higher values of z the Q -dependences of P_{ab} and F^* are different. The exchange interaction is seen to play two roles: it determines an exchange volume in which $S-T_0$ mixing is suppressed (this is the effect of p on the Q -dependence); it is directly responsible for the development of the polarization which takes place in the exchange region and therefore may be expected to depend on the detailed form of $J(r)$. The effects of the magnitude and the form of $J(r)$ as well as the Q -dependence for $z \gg 1$ can be studied by the numerical method discussed in Sect. 3.3.

Qualitative rules for interpretation of CIDEP follow from Eq.(3.12). When the two radicals have identical g -values a multiplet effect is observed which follows the sign rule

$$\Gamma_{m.e.} = -J\mu \begin{array}{l} +:E/A \\ -:A/E \end{array} \quad (3.13a)$$

where μ is + for triplet and R.I. precursors and - for singlet precursors. Note that $(-J)$ is positive when the singlet state has the lowest energy, that both radicals have the same "phase" of the polarization, and that E/A means that the low field lines have negative values and the high field lines have positive values of the polarization. As discussed in Section 5 an E/A multiplet effect in polarization does not necessarily give any lines in emission in the observed spectrum, but the intensity of the low field lines will be lower than the high field lines, cf. Fig. 2.

A net effect is observed when the g -factor difference is so large that the ESR spectra of the two radicals are non-overlapping. Again a simple sign rule can be given

$$\Gamma_{n.e.} = +J(g_1 - g_2) \mu \begin{array}{l} +:A \\ -:E \end{array} \quad (3.13b)$$

where radical 1 is the radical under consideration. The two radicals have opposite polarization, since the total polarization is zero.

The polarization for a R.I. precursor remains to be discussed. It follows from Eq.(3.13) that as $\rho_{SS} = \rho_{T_0 T_0}$ no polarization can be developed for a R.I. precursor. This situation is changed if the radicals are allowed to react spin selectively. Suppose that a fraction F of the radicals reacts in a singlet state, then the remaining radicals will have an "initial" value of $\rho_{SS} - \rho_{T_0 T_0} = -F$. This will lead to a polarization production which can be related to the polarization resulting from unreactive triplet radical pairs by the exact relation

$$P_{ab}(R.I.)/F = P_{ab}(T_0). \quad (3.14)$$

This important relation has been verified by the numerical method [I,II].

3.2 The stochastic Liouville equation.

Consider a system for which the time dependence of the spin density matrix is determined by

$$(\partial/\partial t) \rho(t) = -i H^x(r) \rho(t) \quad (3.15)$$

with a Hamiltonian that depends on a classical time-dependent parameter r . Let the time dependence of r be given by a probability density $P(r,t)$ which satisfies a diffusion equation

$$(\partial/\partial t) P(r,t) = \Gamma_r P(r,t). \quad (3.16)$$

Then the stochastic Liouville equation (SLE) for this system is

$$(\partial/\partial t) \rho(r,t) = -i H^x(r) \rho(r,t) + \Gamma_r \rho(r,t) \quad (3.17)$$

where $\rho(r,t)$ is an operator in the direct product space of the spin operator space and the r -space.

The solution to the SLE (3.17) that satisfies the initial condition

$$\rho(r,0) = \rho(0) P(r,0) \quad (3.18)$$

is related to the required solution $\rho(t)$ of Eq.(3.15) by an integration over r -space

$$\rho(t) = \int_0^\infty dr r^2 \rho(r,t). \quad (3.19a)$$

The initial probability density $P(r,0)$ must be normalized similarly

$$\int_0^\infty dr r^2 P(r,0) = 1 \quad (3.19b)$$

The interesting quantities for CIDNP and CIDEP are the polarizations developed after the termination of all the reencounter cycles. This information is contained in the $t \rightarrow \infty$ limit of $\rho(t)$ which may be calculated conveniently by use of the Laplace transform of $\rho(t)$

$$\tilde{\rho}(s) = \int_0^\infty e^{-st} \rho(t) dt \quad (3.20)$$

and by the relation

$$\lim_{t \rightarrow \infty} \rho(t) = \lim_{s \rightarrow 0} s \tilde{\rho}(s). \quad (3.21)$$

By Laplace transformation of Eq.(3.17) the SLE is obtained in the form

$$[s + i H^x(r) - \Gamma_r] \tilde{\rho}(r,s) = \rho(r,0) \quad (3.22)$$

which is convenient for calculations. Extra terms can be added to this equation to account for reactions and spin relaxation by replacing $-i H^x(r)$ by the superoperators between the brackets

in Eq.(2.12).

3.3 The finite difference method

The problems involved in solving the stochastic Liouville equation (3.22) are connected with the properties of the diffusion operator Γ_r . The diffusion operators employed in [I,II] and [IV - VII] are all differential operators. For example, the diffusion operator is given by

$$\Gamma_r = \frac{D}{r^2} \frac{\partial}{\partial r} r^2 \frac{\partial}{\partial r} \quad (3.23)$$

for continuous free diffusion. The eigenfunctions of the diffusion operators Γ_r are either unknown or have unpleasant properties. Thus it is not feasible to solve the SLE (3.22) by expansion of $\rho(r,t)$ in eigenfunctions of Γ_r .

Numerical solutions to the SLE (3.22) have been obtained by a finite difference technique [I,II,V,VII], i.e, a derivative is written as a finite difference. For example,

$$\frac{\partial^2 P(r,t)}{\partial^2 r} = \frac{1}{\Delta r^2} \left[P(r-\Delta r,t) - 2P(r,t) + P(r+\Delta r,t) \right] \quad (3.24)$$

where Δr is a small but finite increment in r . The application of the finite difference technique is essentially equivalent to transforming the continuous diffusion equation (a Fokker-Planck equation) into a discrete Master equation involving a transition-probability matrix $\bar{\bar{W}}$, coupling $P(r,t)$ between discrete values $P(d+j\Delta r,t)$ where $j = 0, 1, 2, \dots, N$. These discrete values form a column vector $\vec{P}$. Thus

$$\Gamma_r P(r,t) \rightarrow \bar{\bar{W}} \vec{P}(t). \quad (3.25)$$

Figure 14 is a simple illustration of the finite difference description. The original continuous range of r -values has been approximated by $N+1$ selected values, represented by the boxes in the figure. The continuous diffusion has been

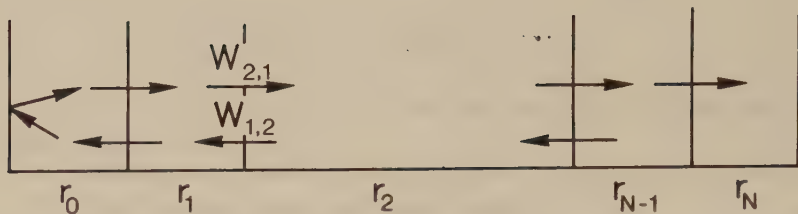


Fig. 14. Illustration of the finite difference description of the relative translational diffusion. Only the discrete values $r_0, r_1, \dots, r_N$ of the relative distance are allowed; diffusion corresponds to jumps between adjacent values of r , called "boxes". The diffusion operator is represented by a tri-diagonal matrix W ; the off-diagonal elements $W_{i,i\pm 1}$ are transition probabilities from "box" $i\pm 1$ to "box" i and are indicated by horizontal arrows. A reflection condition at r_0 and an absorption (or collecting) condition at r_N are indicated.

replaced by jumps into adjacent boxes. The W -matrix is not completely described by the finite difference prescription and additional conditions must be used. Since the radicals are not allowed to diffuse into each other, a reflecting condition is used at $r_0 = d$ (the distance of closest approach). This condition is well known from the continuous description.

An absorption condition must be used at r_N in order to get physically reasonable results, i.e. particles reaching r_N are not allowed to diffuse back. Since the probability of reaching r_0 from r_N is of order r_0/r_N , cf. Eq.(2.10), this is clearly justified when $r_N \gg r_0$. However, the absorption condition employed in the continuous description cannot be used. This absorption condition, $P(r_N, t) = 0$, implies that particles reaching the absorbing wall are "destroyed". As $t \rightarrow \infty$ all particles will be absorbed and consequently all information will be lost (except the information that all particles are absorbed). The perfect boundary condition must prevent radicals from diffusing away without destroying the radicals. Such a boundary condition can be formulated in the

finite difference language [I], cf. Fig. 14,

$$W_{N,N} = W_{N-1,N} = 0. \quad (3.26)$$

This condition guarantees that all particles are collected in the N'th "box" as $t \rightarrow \infty$.

A third condition imposed on W is that the diffusion must not change the total probability, i.e. $(d/dt) \int d^3 \vec{r} P(\vec{r}, t) = \int d^3 \vec{r} \Gamma_{\vec{r}} P(\vec{r}, t) = 0$. This condition leads to the sum rule [I, VII]

$$\sum_i r_i^2 \Delta r_i W_{i,j} = 0 \quad (3.27)$$

which states that the weighted sum of elements of W for each column must be zero. The weight factors are equal to the "degeneracies of the states" which in the present case are the geometrical volume elements. If the diffusion equation in the finite difference form is considered a Master equation then it follows from the properties of Master equations that the left eigenvector of W with eigenvalue zero is the degeneracy vector. This statement is identical with Eq.(3.27). It also follows that the right eigenvector of W with eigenvalue zero is the equilibrium distribution, but this statement is not used for construction of the W matrix. A transformation of $P(r, t)$ will change Eq.(3.27) accordingly. For example, the transformation $P(r, t) \rightarrow r P(r, t)$ employed in [I, II, IV, V, VII] will change the weight factors from $r_i^2 \Delta r_i$ to $r_i \Delta r_i$.

It is advantageous to use different values of Δr_i in different regions. In the exchange region Δr_i must be chosen small enough to get a proper representation of $J(r)$. A much larger value of Δr can be used outside the exchange region and still adequately describe the diffusion. Regions with different Δr values are connected by Eq.(3.27).

When the W-matrix has been constructed the stochastic Liouville equation (3.22) may be written as a matrix equation.

Since $H^{\times}(r)$ is diagonal in r -space and Γ_r in spin operator space their matrix representations in the direct product space are easily found. The W -matrix is singular but $s\bar{I}-\bar{W}$ is non-singular for $s \neq 0$ and the required solution to Eq.(3.22) may then be obtained by a matrix inversion. Since the dimensions of the matrices are typically $4 \times 300 = 1200$ it is necessary to take advantage of the banded nature of the matrices (bandwidth equal to 9). A gaussian elimination program (DGELB in IBM's SSP) has been applied succesfully in [I,II,IV,V].

3.4 Numerical results for CIDEP

As the calculation involves a $t \rightarrow \infty$ limit the electron spin polarization calculated by the finite difference method is denoted P^{∞} . The results of the calculations are given as positive numbers. The sign of the polarization is determined by Eq.(3.13). If nothing else is stated the free diffusion model given by Eq.(3.23) is applied.

The simplest model for the exchange interaction is the contact exchange model defined by

$$J(r) = \begin{cases} J_0 & \text{for } d < r < d + \Delta r_J \\ 0 & \text{for } r > d + \Delta r_J \end{cases} \quad (3.28)$$

with $\Delta r_J < d$. For $Qd^2/D \ll 1$ the finite difference results can be represented by the expression

$$P^{\infty} = \left[\frac{Qd^2}{D} \right]^{\frac{1}{2}} \frac{2J_0\tau_J}{1 + (2J_0\tau_J)^2} \quad (3.29a)$$

which is equivalent to Eq.(3.12). Furthermore, the exchange time τ_J is related to physical parameters

$$\tau_J = d\Delta r_J/D. \quad (3.29b)$$

The effects of more general forms of $J(r)$ have been investigated in [I,II,V,VII], in particular the effects of an exponentially decaying exchange interaction

$$J(r) = J_0 e^{-\lambda(r-d)} \quad (3.30)$$

characterized by the two parameters J_0 and λd . Typical results indicating the dependence of P^∞ on the parameters J_0 and λd are shown in Fig. 15. There is some similarity to the contact exchange model; the main difference is the existence of an almost constant value of P^∞ for large values of J_0 . This important feature has the consequence of permitting significant polarization to develop for large values of J_0 . This asymptotical value of the polarization increases with the extent of the $J(r)$, i.e. with $1/(\lambda d)$. The J -dependence can be

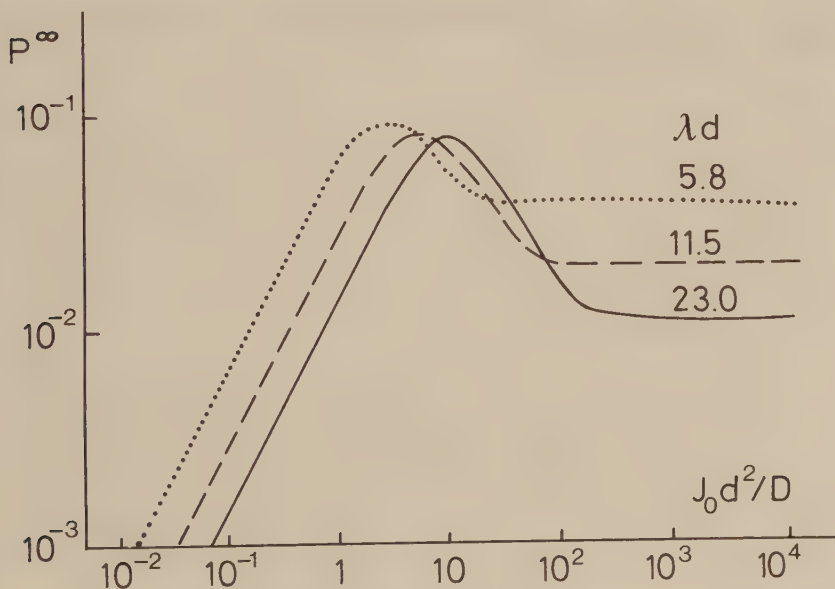


Fig. 15. Numerical results for P^∞ as a function of J_0 and λd ; both axes have logarithmic scale. A value of 3.2×10^{-2} for Qd^2/D has been employed in the calculation.

approximated by

$$P^{\infty}(J_0, \lambda d) \propto \frac{2J_0\tau_J + 1.5(2J_0\tau_J)^2/(\lambda d)}{1 + (2J_0\tau_J)^2} \quad (3.31)$$

in which the exchange time τ_J is well represented by

$$\tau_J = (d^2/D)(\lambda d)^{-1}[1 + (\lambda d)^{-1}]. \quad (3.32)$$

The J -dependence of P^{∞} , for other forms of $J(r)$ than the exponential, has been investigated in [II]. For $Qd^2/D \ll 1$ the numerical results can be incorporated into the general expression

$$P^{\infty} = (Qd^2/D)^{\frac{1}{2}} 2J_0\tau_J \quad \text{for } 2J_0\tau_J \ll 1, \quad (3.33)$$

the factor $(2J_0\tau_J)$ is independent of Q and is related to a general form of $J(r)$ by

$$2J_0\tau_J = 2 \int_d^{\infty} rJ(r)dr/D. \quad (3.34)$$

This unpublished expression is very similar to a relation for the reaction time (or reaction volume) in classical reaction kinetics, cf. [10]. The expressions (3.29b) and (3.32) for the exchange time for specific models are special cases of the general expression (3.34).

The J -dependence of P^{∞} for $2J_0\tau_J > 1$ is complex and has not been expressed in a relation covering a general form of $J(r)$; only for the exponential and contact exchange models the complete J -dependence has been given in closed form, Eqs. (3.29) and (3.31). A constant asymptotical value of P^{∞} is obtained for an exponentially decaying $J(r)$ of "extent" $\leq 5d$. For $J(r)$'s of longer extent or of slower decay, e.g. r^{-6} or r^{-12} , the polarization P^{∞} increases with J_0 .

The Q -dependence of P^{∞} differs from the square root dependence for values of Qd^2/D that are an order of magnitude smaller than those for which similar departures are observed

for the CIDNP quantity F^* . Pronounced deviations from the square root dependence are observed for values of Qd^2/D as low as 10^{-2} , cf.[VII], so a more accurate expression for the Q -dependence is needed. In the present work it is found that the combined J and Q dependences of P^∞ for an exponential $J(r)$ are well represented by

$$P^\infty = \frac{p}{1-p} e^{-z} \sin z \frac{2J_0\tau_J + 1.5(2J_0\tau_J)^2/(\lambda d)}{1 + (2J_0\tau_J)^2} \quad (3.35a)$$

with

$$z = (Qd^2/D)^{\frac{1}{2}} (1-p)/p \quad (3.35b)$$

and

$$p = 0.6 - 0.1 \frac{(2J_0\tau_J)^2}{1 + (2J_0\tau_J)^2} \quad (3.35c)$$

The effects of intermolecular forces between the radicals have been studied in [II, VII] by application of the diffusion operator (the Smoluchowski operator)

$$\Gamma_r = r^{-2} (\partial/\partial r) r^2 D \left[(\partial/\partial r) + (dU/dr)/(kT) \right] \quad (3.36)$$

where $U(r)$ is the potential energy between the radicals. To lowest order the effect of the potential is to replace d by df^* (the effective distance of closest approach) and τ_J by $\tau_J \exp(-U(d)/kT)$. These replacements are expected from the theory of reaction kinetics (see for example [10]). By application of Eqs.(3.35) for $z \ll 1$ and the above replacements it is predicted that

$$P^\infty/P_0^\infty = \exp(-U(d)/kT) \text{ for } 2J_0\tau_J \ll 1 \quad (3.37a)$$

and

$$P^\infty/P_0^\infty = 1 \text{ for } 2J_0\tau_J \gg 1 \quad (3.37b)$$

where P_0^∞ is the value in the absence of $U(r)$. The calculated trends are in accordance with these predictions, but Eq.(3.37a) overestimates the actual effect and Eq.(3.37b) underestimates the effect. For $2J_0\tau_J \gg 1$ the actual effect on P^∞ is less than 50% enhancement for repulsive forces and less than a factor three reduction for attractive forces. These effects have been experimentally observed [18,19].

Dynamical interactions between the radicals affect the relative motion but do not affect the potential energy. A particular class of such interactions may be represented by r -dependent diffusion constants $D(r)$ for the relative diffusion; the diffusion operator may be written as

$$\Gamma_r = r^{-2}(\partial/\partial r)r^2D(r) \left[(\partial/\partial r) + (dU/dr)/kT \right]. \quad (3.38)$$

It was found in [V] that the use of Eq.(3.38) instead of Eq.(3.36) resulted in minor changes of P^∞ only (less than a factor of two). This result is consistent with the discussion leading to Eqs.(3.37).

The effects of spin dependent diffusion on the polarization have been studied in [II] and [VII]. For the spin independent diffusion models the effect of the diffusive motion (the bath) on the spin system was considered. Since the spin Hamiltonian depends on r and r is determined by the diffusive motion, it follows immediately that the spin system depends on the bath. This one way communication bath $\rightarrow$ system is the basis of most relaxation theories, i.e. it is assumed that the bath is so "large" that it remains unaffected of changes in the "small" system to which it is coupled. A more consistent description must include the "back reaction" (system $\rightarrow$ bath) as well as the bath $\rightarrow$ system interaction.

In the discussion of Fig.4 it was emphasized that the exchange interaction could give rise to an attraction of singlets and a repulsion of triplets. Thus in the diffusion operator (3.36) an attractive potential ($=-J(r)$) must be

included for singlets but a repulsive potential ($=+J(r)$) for triplets. Then the potential $V(r)$ in the diffusion operator (3.36) becomes a superoperator in spin space. The correct potentials for singlets (ρ_{SS}) and triplets (ρ_{TT}) are obtained by the identification

$$U(r) = \frac{1}{2} H(r)_+ \quad (3.39)$$

where H_+ is the anti commutator superoperator, i.e. $A_+B=[A,B]_+=AB+BA$. Equation (3.39) implies that the off-diagonal elements ρ_{ST} diffuse in a potential equal to half the sum of the singlet and triplet potentials; this potential is zero for the special form of the exchange interaction used in this presentation. It has later been proved [20] that Eq.(3.39) is the correct form of the spin dependent potential for any r -dependent Hamiltonian. It is noteworthy that spin dependent diffusion results in spin relaxation towards the thermal equilibrium distribution while spin independent diffusion leads to an even distribution of the spin states (the $T \rightarrow \infty$ distribution).

The form of the superoperator $K(r)$ for the recombination process introduced in Eq.(2.15b) is seen to be closely related to the above spin-dependent diffusion model. The numerical results [II] for P^∞/F using Eq.(2.15b) for $K(r)$ agree with those obtained for the spin dependent diffusion model except for $F < 10^{-2}$ where rather drastic changes occur. The spin dependent diffusion model is self-consistent, there is no need for irreversible reaction terms like $K(r)$. In this model a reaction is a trapping in a potential and no particles are lost to the system. Consequently the polarization for R.I. pairs cannot be calculated by a $t \rightarrow \infty$ limit; the radicals remain "reacted" for a finite time only.

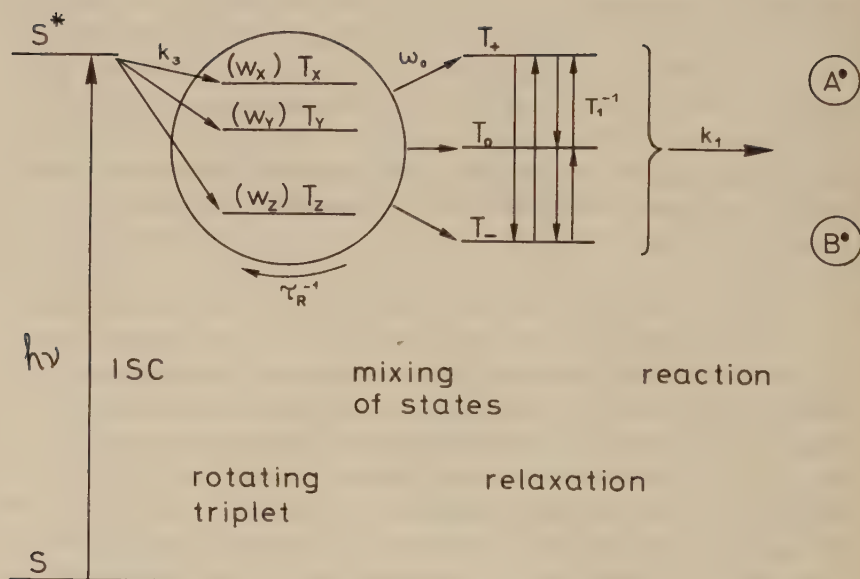


Fig. 16. The sequence of processes involved in the triplet mechanism. The various processes are indicated by arrows and explained by the text at the bottom of the figure. The rates of the processes are given by the smaller letters near the process arrows. The symbols in parentheses, e.g. (w_x) , indicate the relative populations of the levels caused by the intersystem crossing (ISC). For more details, see text.

4

THE TRIPLET MECHANISM

4.1 Physical background

The sequence of processes involved in the triplet mechanism (TM) is illustrated in Fig. 16. Initially, the precursor molecule is in a singlet ground state S ; then it is photo-excited to an excited singlet state S^* from which there is intersystem crossing (ISC) into the triplet state (T_x, T_y, T_z). The ISC is due to spin-orbit interaction and takes place in accordance with selection rules in the molecular frame (see for example [21]), i.e. the zero field states T_x, T_y, T_z are populated preferentially by the ISC. However, in the strong magnetic field of the spectrometer the spin eigenstates are not the molecular states T_x, T_y, T_z but are approximately equal to the laboratory high field states T_+, T_0 , and T_- . These states are, of course, just linear combinations of the zero field states. In order to find the populations of the true eigenstates the states must be expressed as linear combinations of the zero field states. The linear combinations depend on the orientation of the molecular axes to the magnetic field. All orientations are equally probable for a molecule in a liquid. Furthermore the molecule is tumbling, making the linear combinations time dependent, and the effects of this tumbling must be considered. Finally, the triplet spin lattice relaxation tends to destroy the generated triplet spin polarization before the reaction transfers the polarization to the radicals, cf. Fig. 7. Thus the rate of the reaction yielding the radical pair as products becomes important as well.

4.2 A qualitative description

The transfer of polarization from the zero field states to the true eigenstates is considered first. The zero field states are eigenstates of the zero field Hamiltonian

$$H_{zf} = D (S_z^2 - \frac{1}{3}S^2) + E (S_x^2 - S_y^2) \quad (4.1)$$

where the operators are expressed in the molecular frame. Many systems have $|D| \gg |E|$ and can be assumed to be axially symmetric. The eigenstates of H_{zf} (T_x , T_y , and T_z) are also eigenstates of the operators S_x , S_y , and S_z , respectively, with eigenvalues zero.

When an external magnetic field $\vec{B}$ is applied to the system the Zeeman interaction $H_z \propto \vec{B} \cdot \vec{S}$ must be included in the Hamiltonian and thus the eigenstates are changed. The exact forms of the eigenstates are not needed for a qualitative description. A discussion of the polarization transfer from the zero field states to the true eigenstates can be based on the energy level diagrams for the system. These diagrams are shown in Fig. 17 and can be constructed by the following general arguments.

If the magnetic field is applied along one of the molecular axes (say z) then the corresponding zero field state (T_z) remains an eigenstate of the Hamiltonian with unchanged energy. This is because the projection of the spin on the quantization axis is zero, i.e. $H_z |T_z\rangle \propto S_z |T_z\rangle = 0$. Another important point is that the remaining states (T_x , T_y) are coupled by $H_z \propto S_z$, i.e. $\langle T_x | S_z | T_y \rangle \neq 0$. This follows, for example, by noting that S_z is the generator of infinitesimal rotations about the z -axis and that T_y is mixed with T_x by such a transformation. The energy levels of two states coupled by a non-vanishing perturbation (H_z) cannot cross as the strength of the perturbation is varied. Therefore the energy levels of the mixed states (T_x , T_y) cannot cross as the magnetic field is varied. Furthermore, the

Zeeman interaction is dominant for high magnetic fields and the eigenstates become the high field states T_+ , T_0 , and T_- with eigenvalues proportional to $+B$, 0 , and $-B$, respectively. Figure 17 is now readily constructed.

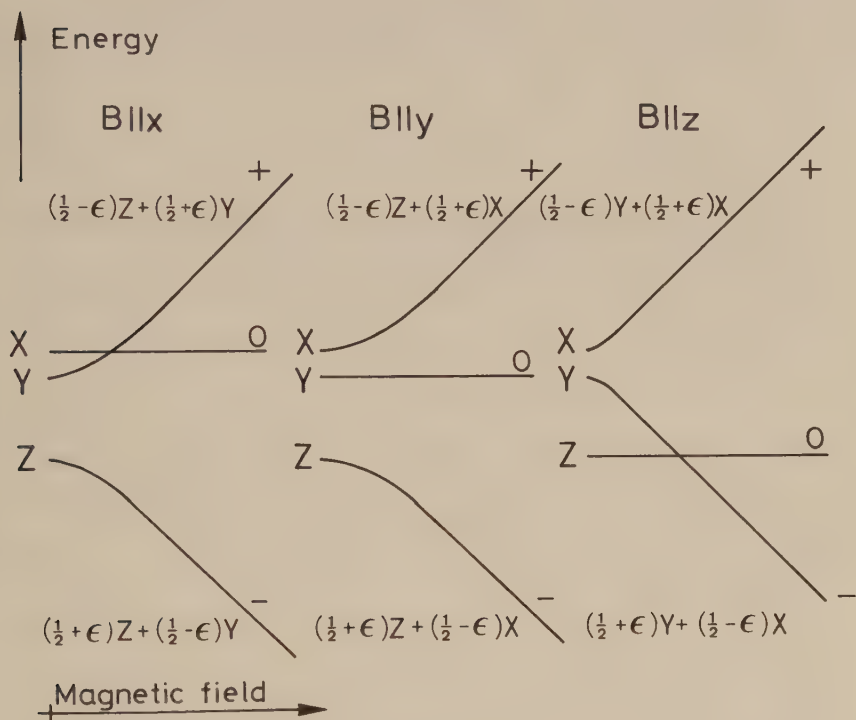


Fig. 17. Energy level diagrams for a triplet system as a function of the magnitude of a magnetic field applied along the directions of the molecular x , y , and z axes, respectively. The magnetic field is zero on the left-hand side of each subfigure and increases to the right. The zero field states are denoted X , Y , and Z . In the presence of a magnetic field the eigenstates with highest and lowest energy are denoted $+$ and $-$, respectively. The indicated linear combinations give the conditional probabilities, cf. Eq.(4.2); for example, $(\frac{1}{2}-\epsilon)Z + (\frac{1}{2}+\epsilon)Y$ for state $+$ means that $|\langle +|Z \rangle|^2 = \frac{1}{2} - \epsilon$ and $|\langle +|Y \rangle|^2 = \frac{1}{2} + \epsilon$.

The problem of finding the populations of the true eigenstates (which result from a preferential population of the zero field states by the ISC) is most easily handled for a static system, i.e. the orientation of the molecular axes relative to the magnetic field is independent of time. Suppose that only one of the zero field states, the T_α -state ($\alpha = x, y, \text{ or } z$), is populated by the ISC then the population of the eigenstate $|E_i(B)\rangle$ ($i=-, 0, +$) is equal to

$$\text{Prob } \{E_i(B) | T_\alpha\} = |\langle E_i(B) | T_\alpha \rangle|^2. \quad (4.2)$$

This is the conditional probability of finding the system in state $|E_i(B)\rangle$ when it is known to be in the T_α -state. The population of $|E_i(B)\rangle$ for a general situation is then given by

$$\text{Prob } \{E_i(B)\} = \sum_{\alpha} \text{Prob } \{E_i(B) | T_\alpha\} w_{\alpha} \quad (4.3)$$

where w_{α} is the fractional population of the zero field state T_{α} by the ISC. The w 's are the relative rates of the ISC into the zero field states and satisfy

$$\sum_{\alpha} w_{\alpha} = w_x + w_y + w_z = 1. \quad (4.4)$$

The conditional probabilities given by Eq.(4.2) depend on the relative orientation of the molecule with respect to the magnetic field. All orientations are equally probable for liquid systems and thus Eq.(4.2) must be averaged over all orientations. This average value can be estimated as one third of the sum of the values for the magnetic field along the three molecular axes. For each of the three cases

($B||x, B||y, B||z$) the conditional probabilities are shown in Fig. 17; the notation $(\frac{1}{2}+\epsilon)T_z + (\frac{1}{2}-\epsilon)T_y$ for a specific eigenstate $|-\rangle$ indicates that $|\langle - | T_z \rangle|^2 = \frac{1}{2} + \epsilon$ and $|\langle - | T_y \rangle|^2 = \frac{1}{2} - \epsilon$. The eigenstates $|E_i(B)\rangle$ with $i=-, 0, +$ are denoted simply as $|-\rangle, |0\rangle, |+\rangle$.

The parameter ϵ depends on B and clearly $\epsilon(B=0)=\frac{1}{2}$. As two

states mixed by a perturbation will contribute equally to the eigenstates in the limit of infinitely large perturbation it follows that $\epsilon(B \rightarrow \infty) = 0$.

With the aid of Fig. 17 the orientational average populations of the energy states can be estimated. Actually, it is the difference in populations of the lowest and highest energy states that is of interest. When the magnetic field is so large that the energy states are approximately equal to the high field states T_+ , T_0 , T_- then all radicals resulting from T_+ and T_- precursor molecules have spin up and down, respectively; radicals from T_0 -precursors are unpolarized, cf. Fig. 7. The polarization P of the radicals is defined as the excess population of the spin down state, cf. Eq.(3.1a), and is thus equal to the difference in populations of the lowest and highest energy states. The polarization is obtained by Fig. 17 and Eq.(4.3) as

$$P = \epsilon \frac{4}{3} (w_z - w_x). \quad (4.5)$$

For an axially symmetric system the T_x and T_y states are degenerate and equally populated by the ISC ($w_x = w_y$). Thus w_x is not a physical observable whereas w_z and $w_x + w_y$ are. Equation (4.5) should therefore be written as

$$P = r \epsilon \frac{4}{3} \quad (4.6)$$

where r gives the anisotropy of the ISC

$$r = w_z - \frac{1}{2}(w_x + w_y). \quad (4.7)$$

When the zero field interaction is much smaller than the Zeeman interaction, the parameter ϵ can be estimated by perturbation theory. The eigenstates $|+\rangle$, $|0\rangle$, and $|-\rangle$ are approximately equal to the high field states T_+ , T_0 , and T_- , e.g.

$$|-\rangle = |T_-\rangle - \sum_{j=0,+} |T_j\rangle \frac{\langle T_j | H_{zf} | T_- \rangle}{E^0(T_j) - E^0(T_-)}. \quad (4.8)$$

As the matrix elements of H_{zf} are of order D , cf. Eq.(4.1), and the energy differences in the denominator are of order ω_0 (the Larmor frequency for the triplet) then the correction term in Eq.(4.8) is of order D/ω_0 . Thus

$$\langle T_\alpha | - \rangle = \langle T_\alpha | T_- \rangle - (D/\omega_0) \sum_{j=0,+} \langle T_\alpha | T_j \rangle \text{const}(j) \quad (4.9)$$

where T_α ($\alpha=x,y,z$) is a zero field state. As D/ω_0 is the only term in Eq.(4.9) which depends on the magnetic field B it follows that

$$|\langle T_\alpha | - \rangle|^2 = |\langle T_\alpha | T_- \rangle|^2 - (D/\omega_0) \text{constant} \quad (4.10)$$

to first order in D/ω_0 . The constant in Eq.(4.10) is of order one and is independent of B but may depend on the states involved. By comparison with Fig. 17 it is observed that

$$\epsilon \propto D/\omega_0. \quad (4.11)$$

Notice that only radicals originating from the triplet state can be polarized. By defining p as the fraction of radical pairs originating from the triplet state the conclusions derived so far may be summarized as

$$P \propto rp(D/\omega_0) \quad (4.12)$$

where the constant of proportionality is of order one. This constant is found to be $8/15$ by the quantitative treatments [6,22,VI]. This terminates the treatment of a static, randomly oriented system with no spin lattice relaxation.

Triplet spin lattice relaxation relaxes the populations of the triplet states towards the equilibrium distribution which essentially is an even distribution. The rate of relaxation is T_1^{-1} where T_1 is the triplet spin lattice relaxation time. If the reaction (triplet precursor $\rightarrow$ radical pair) proceeds with rate constant k_1 then the fraction $k_1/(k_1+T_1^{-1})$ of the original triplet polarization will be

transferred to the radicals; the remaining fraction of the triplet polarization will be destroyed by spin lattice relaxation. The polarization can then be written as

$$P = rp \frac{8}{15} \frac{D}{\omega_0} \frac{k_1}{k_1 + T_1^{-1}} \quad (4.13)$$

Usually $T_1 \approx 1$ ns in liquids. Thus the triplet lifetime k_1^{-1} must be less than ~ 10 ns if significant polarization is to be transferred to the radicals. Probably, electron and hydrogen transfer reactions are the only reactions fast enough to satisfy this condition.

The diffusive rotational motion (tumbling) of the molecule is characterized by the rotational correlation time τ_R . The triplet spin lattice relaxation is generated by the rotational modulation of the zero field interaction and thus T_1 depends on τ_R . There is, however, one more effect of this motion. When the rate of the rotational motion (τ_R^{-1}) is larger than the rate of precession (ω_0) of the spins then the spins cannot follow the rotational motion and therefore do not feel the presence of the zero field interaction. The eigenstates become effectively the true high field states. These states, however, have $\epsilon = 0$, cf. Fig. 17, and thus there is no radical polarization. This averaging-out of the polarization can be qualitatively accounted for by multiplication of Eq. (4.13) by a function that is equal to one for $\tau_R^{-1} \ll \omega_0$ (slow motion) and zero for $\tau_R^{-1} \gg \omega_0$ (fast motion). One possible choice is given by the relation

$$P = rp \frac{8}{15} \frac{D}{\omega_0} \frac{k_1}{k_1 + T_1^{-1}} \frac{\omega_0^2}{\omega_0^2 + \tau_R^{-2}} \quad (4.14)$$

The picture of a spin precessing about an effective field used above is convenient for a discussion of the last effect too. Just after an intersystem crossing into the T_z -state (for example) the spin is pointing (i.e. quantized) in direction of the molecular z-axis. However, the true quantization axis is close to the direction of the magnetic field and thus the spin will "move" into this direction where it will be polarized

with respect to the magnetic field. The rate of change of direction is equal to the rate of precession ω_0 of the spins. If the reaction of the triplet molecule takes place before the spin has changed its direction (i.e. $k_1 \gg \omega_0$) then the resulting radicals will be unpolarized. A collection of spins pointing in random directions is not polarized with respect to a fixed direction. The polarization appears after the quantum mechanical mixing of states (change of quantization axis) only. This effect can be incorporated by multiplication of the above result Eq. (4.14) with $\omega_0^2/(\omega_0^2 + k_1^2)$. The final expression for the radical polarization

$$P = r_p \frac{8}{15} \frac{D}{\omega_0} \frac{k_1}{k_1 + T_1} \frac{\omega_0^2}{\omega_0^2 + \tau_R} \frac{\omega_0^2}{\omega_0^2 + k_1^2} \quad (4.15)$$

is remarkably close to the expressions obtained by the quantitative treatments [22, VI] and it incorporates the effects of all relevant physical processes.

4.3 Quantitative results.

The stochastic Liouville equation (SLE) may be used for a theoretical description that is exact for the assumed model [VI, VII] and it may be solved numerically to any degree of accuracy [VI, VII]. It may also be solved approximatively by a degenerate perturbation technique [VI, VII] valid for $D/\omega_0 \ll 1$. By comparison with the numerical results it is found that the approximate, analytic expression obtained by the perturbation analysis is accurate to 10% or better for $D^2 \lesssim \frac{1}{2}(\omega_0^2 + \tau_R^{-2})$. The effect of having the triplet polarization relax to the equilibrium value $P_{eq}^{(3)}$ rather than to zero (as was assumed in the above qualitative derivation) is included in the perturbation treatment. The results of the perturbation treatment are

$$P^\infty = P'^\infty + \frac{T_1^{-1}}{k_1 + T_1} P_{eq}^{(3)} \quad (4.16a)$$

where

$$\frac{P^{\infty}}{pr} = \frac{4D}{15} \left\{ \frac{\omega_0}{\omega_0^2 + \tau_R^{-2}} \left[\frac{k_1}{k_1 + T_1^{-1}} - \frac{(k_1 + 2\tau_R^{-1})k_1}{\omega_0^2 + (k_1 + \tau_R^{-1})^2} \right] + \frac{4\omega_0}{4\omega_0^2 + \tau_R^{-2}} \left[\frac{k_1}{k_1 + T_1^{-1}} - \frac{(k_1 + 2\tau_R^{-1})k_1}{4\omega_0^2 + (k_1 + \tau_R^{-1})^2} \right] \right\} \quad (4.16b)$$

$$r = w_z - \frac{w_x + w_y}{2} - \frac{D}{2\omega_0} P_{eq}^{(3)}, \quad (4.16c)$$

and

$$T_1^{-1} = \frac{2}{15} D^2 \left[\frac{\tau_R^{-1}}{\omega_0^2 + \tau_R^{-2}} + \frac{4\tau_R^{-1}}{(2\omega_0)^2 + \tau_R^{-2}} \right]. \quad (4.16d)$$

Note the similarity with Eq. (4.15) obtained by the qualitative method. An expression equivalent to Eqs. (4.16) has been obtained by Atkins and Evans (22) by a different approximate technique. These authors also considered the case $E \neq 0$.

The possibility of obtaining information about the zero field parameter D and the triplet lifetime k_1^{-1} by measuring the triplet polarization $P^{\infty}(\text{TM})$ has been investigated in [VIII]. Figure 18 shows $P^{\infty}(\text{TM})/(rp)$ as a function of k_1^{-1} for a series of different values of D and for two rotational correlation times τ_R , which are supposed to be representative for the investigated radical p-benzoequinone (PBQ) dissolved in ethylene glycol and isopropanol, respectively. The experimental values of $P^{\infty}(\text{TM})$ are shown by the horizontal lines.

The analysis based on Fig. 18 goes as follows: In order to get theoretical values of $P^{\infty}/(rp)$ equal to or larger than the experimental values it is necessary that $|D| \geq 730\text{G}$ and that the triplet lifetime k_1^{-1} is in the range 10^{-8} - 10^{-10}s . Since the polarization is linear in (rp) it follows that $|rpD| > 730\text{G}$. The values of r are limited to the interval $[-\frac{1}{2}, 1]$ when the small contribution from $P_{eq}^{(3)}$ is neglected. The values of p belong to $[0, 1]$. As the experimental polarization is negative it follows that $rD < 0$, cf. Eqs. (4.16). If $r > 0$ (i.e. the T_z -state is populated preferentially) then $D < 0$ and $|D| \geq 730\text{G}$. If $r < 0$ then $D > 0$ and $D \geq 1460\text{G}$.

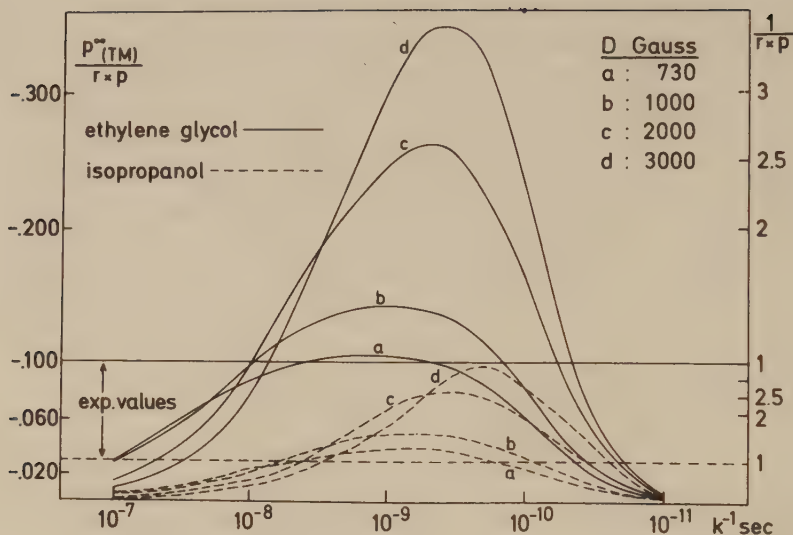


Fig. 18. Polarization by TM as a function of the triplet lifetime k_1^{-1} for values of τ_R representative of PBQ dissolved in ethylene glycol and isopropanol. Letters a-d on the curves give D in gauss; these values may be converted into cm^{-1} by multiplication by 9.34×10^{-5} . The magnetic field is 3300G. Horizontal lines show the experimental values. The curves are calculated from Eqs.(4.16). For $pr \neq 1$ displace the experimental line to nearest value for $1/(pr)$ on the right-hand scale and divide the values on the left-hand $P^{\infty}(\text{TM})$ scale by $1/(pr)$. From VIII.

It may be concluded that most likely $(rp)D \approx 730\text{G}$ and the triplet lifetime is of order of 10^{-9}s . These conclusions are consistent with the diverging values of D (730G and 1890G) obtained by liquid helium temperature measurements with PBQ incorporated in host crystals (see [VIII]). The triplet lifetime is in agreement with the inability to observe the triplet in flash photolysis experiments with 10^{-8}s time resolution.

It is worth emphasizing that the accuracy of the above analysis is determined by the accuracies of the estimated value of τ_R and by the experimental value of $P^{\infty}(\text{TM})$. The

accuracy of $P^\infty(\text{TM})$ is often limited to 50%, cf. the following sections, and the use of the Stokes-Einstein relation for an estimation of τ_R is known to be uncertain for small particles.

5

TIME DEPENDENCE OF ESR INTENSITIES

5.1 Introduction

Transient free radicals may be observed by ESR for steady state systems as well as for time dependent systems. For steady state systems the ESR spectrum is recorded as usually and the absorption signal is proportional to the number of radicals in the sample multiplied by the "steady state value of the polarization". This polarization value depends upon a number of processes taking place in the steady state system, e.g. the continuous production of radicals and polarizations, the disappearance of radicals, and the electron spin lattice relaxation.

In a time-resolved ESR experiment the ESR signal is recorded for each hyperfine line as a function of time. In a pulse experiment the radical producing source is applied for a short time and the signal is recorded until the radicals produced by the pulse have disappeared. In a modulated light experiment [VIII] the light source is modulated periodically and the time dependence of the changes in the ESR signal caused by the modulation is recorded. The time dependent intensity curves contain much more information than just the values of the steady state polarization. However, in order to extract the information a careful curve fitting is needed. This curve fitting may be performed conveniently by application of a theoretical description developed in [III] and [XI]. The theory is based on modified Bloch equations and has been applied successfully to extraction of quantitative information from experimental data [VIII].

5.2 The modified Bloch equations

In a description based on the Bloch equations the absorption signal is proportional to the y-component in the rotating frame of the magnetization $\vec{M}$ and the dispersion signal is proportional to the x-component. It is assumed that each hyperfine line is associated with a characteristic magnetization which is independent of the other hyperfine lines. Thus each line can be treated separately.

The Bloch equations are approximate rate equations for the magnetization. In the frame following the rf-field (the rotating frame) these equations are

$$d\vec{M}/dt = \vec{L}\vec{M}(t) + T_1^{-1}\vec{M}_{eq} \quad (5.1a)$$

where

$$\vec{L} = \begin{bmatrix} -T_2^{-1} & \Delta\omega & 0 \\ -\Delta\omega & -T_2^{-1} & -\omega_1 \\ 0 & \omega_1 & -T_1^{-1} \end{bmatrix} \quad (5.1b)$$

and $\vec{M}_{eq}$ is the equilibrium value of the magnetization in the presence of a static magnetic field in the z-direction, i.e.

$$\vec{M}_{eq} = nP_{eq} \begin{bmatrix} 0 \\ 0 \\ 1 \end{bmatrix} \quad (5.2)$$

where n is the number of radicals in the sample and P_{eq} is the equilibrium polarization. The other quantities in Eqs.(5.1) have their usual meanings. T_1 and T_2 are the longitudinal (spin-lattice) and transverse relaxation times; $\Delta\omega$ is the frequency of the rf field relative to the ESR transition frequency (i.e. $\Delta\omega=0$ on resonance), and ω_1 gives the strength of the rf field ($\omega_1=\gamma H_1$).

The Bloch equations (5.1) have been generalized to account for chemical reactions and polarization productions [III, XI]. The resulting equations, which may be called modified or generalized Bloch equations, are

$$d\vec{M}/dt = \vec{L}\vec{M}(t) - T_C^{-1}(t)\vec{M}(t) + \vec{F}(t) \quad (5.3)$$

where

$$\vec{F}(t) = \begin{bmatrix} 0 \\ 0 \\ f_a(t) \end{bmatrix} \quad (5.4)$$

and

$$f_a(t) = P_{eq} T_1^{-1} n(t) + P_a(I) k_o(t) + P_a k_2 F n_B(t) n(t). \quad (5.5)$$

The interpretation of the terms in Eqs. (5.3) is as follows: the first term on the right-hand side describes the time dependence due to the interactions with the magnetic fields and due to spin relaxation; this is the main term in the regular Bloch equations (5.1). The second term in Eq. (5.3) is a relaxation term describing the lifetime broadening caused by the chemical reaction of the radicals; the instantaneous chemical lifetime $T_C(t)$ is defined as the reciprocal of the relative rate of radical disappearance $-n(t)^{-1} dn/dt$. The last term in Eq. (5.3) contains contributions from the three polarization terms defined in Eq. (5.5).

The first term in Eq. (5.5) is analogous with the $T_1^{-1} M_{eq}$ term in Eqs. (5.1) and (5.2) and expresses that the z-component of magnetization relaxes towards the instantaneous "equilibrium" magnetization $P_{eq} n(t)$; $n(t)$ is the instantaneous number of the investigated radical in the sample.

The second term in Eq. (5.5) represents an initial polarization production; $k_o(t)$ is the rate of formation of the

radicals and $P_a(I)$ is the initial polarization of the radical in hyperfine state a. This initial polarization may be due to the triplet mechanism (cf. Sect.5) as well as to the radical pair mechanism (cf. Sect.4). The reason why the RPM may give rise to initial polarization is that polarization by RPM is generated within approximately 10^{-8} s (cf. Appendix) which is a short time in comparison with other processes of the radical. The polarization thus appears as an initial polarization. Initial polarization can also be polarization transferred from a primary to a secondary radical. If the radical under investigation is a secondary radical then its initial polarization will be equal to the polarization of the primary radical at the instant of reaction and $k_0(t)$ will be the rate of the transfer reaction.

The last term in Eq.(5.5) represents the polarization production resulting from a termination reaction, i.e. a reaction with a radical B. If the radicals react with more than one type of radical B then this term should be summed over B. As discussed in Sect's 1 and 4 such a reaction is spin selective and thus generates polarization by the RPM. The experimentally observable rate constant is written as k_2F where k_2 is the rate constant for a diffusion controlled reaction and F is the probability of reaction per collision, cf. [10]. The polarization P_a is the polarization resulting from unreactive triplet radical pairs, cf. Eq.(3.14).

Equations (5.3) - (5.5) are valid for all kinetic models. A typical kinetic rate equation is

$$dn/dt = k_0(t) - k_1n(t) - k_2Fn_B(t) n(t), \quad (5.6)$$

but the theoretical description is not limited to systems described by simple rate equations such as Eq.(5.6).

5.3 General solutions

The application of the modified Bloch equations (5.3) to a description of experimental results is considerably facilitated by the use of the general solutions obtained in [III, VIII and XI].

For the sake of simplicity assume that the lifetime of the radicals is much longer than the spin lattice relaxation time ($T_C(t) \gg T_1$). The term $T_C^{-1}(t)\vec{M}(t)$ in Eq.(5.3) can then be neglected. Laplace transformation and rearrangement of the resulting rate equations yield

$$\vec{M}(s) = \vec{L}(s)^{-1} [\vec{M}(0) + \vec{F}(s)] \quad (5.7)$$

where

$$\vec{L}(s) = -\vec{L} + s\vec{I} \quad (5.8)$$

and $\vec{M}(0)$ is the initial magnetization. By inverse Laplace transformation of Eq.(5.7) the general, although formal, result

$$\vec{M}(t) = \vec{g}(t)\vec{M}(0) + \int_0^t \vec{g}(t')\vec{F}(t-t')dt' \quad (5.9)$$

is obtained. The quantity $\vec{g}(t)$ is the inverse Laplace transform of $\vec{L}(s)^{-1}$

$$\vec{g}(t) = \mathcal{L}^{-1}\{\vec{L}(s)^{-1}\} = \exp(\vec{L}t). \quad (5.10)$$

Equation (5.10) indicates the two common ways of calculating $\vec{g}(t)$: (1) direct inversion of $L(s)$ by use of the adjoint matrix followed by an inverse Laplace transformation; (2) introduction of the transformation that diagonalizes $\vec{L}$, i.e. by solving the eigenvalue problem. The former method was used by Torrey [23] who first considered time dependent solutions to the Bloch equations (5.1). The latter method is convenient for numerical solutions.

It is convenient to introduce the following definitions

$$g_Y(t) = g(t)_{YZ} \quad (5.11a)$$

$$g'_Z(t) = g(t)_{YY} \quad (5.11b)$$

and

$$G_Y(t) = T_1^{-1} \int_0^t g_Y(t') dt' \quad (5.12)$$

Note that the functions $g_Y(t)$, $g'_Z(t)$, and $G_Y(t)$ are determined solely by the matrix $\bar{L}$ and thus independent of the kinetics of the systems. For a few experimental conditions the functions $g(t)$ may be expressed in analytic form, cf. [III, XI]. For example, for $T_1=T_2$ and $\Delta\omega=0$ (on resonance)

$$g_Y(t) = \sin(\omega_1 t) \exp(-t/T_1) \quad (5.13a)$$

$$g'_Z(t) = \cos(\omega_1 t) \exp(-t/T_1) \quad (5.13b)$$

$$G_Y(t) = \{1 - \exp(-t/T_1) [\cos(\omega_1 t) + \sin(\omega_1 t)/(\omega_1 T_1)]\} \omega_1 T_1 / (1 + \omega_1^2 T_1^2) \quad (5.13c)$$

Equations (5.13) illustrate the general characteristic features of the time dependence of $g_Y(t)$ and $G_Y(t)$: $g_Y(t)$ goes from zero to a maximum value in a time of order T_1 or ω_1^{-1} (which ever is shortest) and then decays back to zero during the following $3T_1$ seconds; $G_Y(t)$ increases from zero to a constant value during a time interval of order $3T_1$.

The absorption signal can now be written as

$$M_Y(t) = y_0 g'_Z(t) + m_0 g_Y(t) + \int_0^t g_Y(t') f(t-t') dt' \quad (5.14)$$

This expression can be simplified by noting that the time dependence of two of the terms in $f(t)$ arises from $n(t)$ cf. Eq. (5.5), and that this time dependence is much slower than that

of $g(t)$, which varies essentially as $\exp(-t/T_1)$, cf. Eq.(5.13). These terms can then be considered constant in the integration range and Eq.(5.14) can be approximated by

$$M_Y(t) = y_O g'_Z(t) + m_O g_Y(t) + P_a(I) \int_0^t g_Y(t-t') k_O(t') dt' + [P_{eq} n(t) + P_a T_1 k_2 F n_B(t) n(t)] G_Y(t). \quad (5.15)$$

Equation (5.15) is the starting point for a description of the time dependence of the absorption signal for a system with a slow radical decay. No further simplifications are possible before the experimental conditions are specified so that the functions $g(t)$ and $k_O(t)$ are known; $k_O(t)$ is proportional to the intensity of the radical producing source. An important feature of the general solution (5.15) is that the time dependence due to the kinetics is contained in $n(t)$ and is completely separated from the relaxational behaviour which is included in the functions $g_Y(t)$ and $g'_Z(t)$.

The effect of the spectrometer response must always be considered in a time resolved experiment. The observed signal $I(t)$ is related to the true absorption signal $M_Y(t)$ by the convolution

$$I(t) = \int_{-\infty}^t M_Y(t') r(t-t') dt' \quad (5.16)$$

where $r(t)$ is the spectrometer response to a delta function input signal, and linear response has been assumed.

5.4 Pulse experiments

In a pulse experiment the radicals are produced by a pulsed source which is applied for a short time T_p . The time between consecutive pulses is sufficiently long for all radicals to disappear before application of the next pulse. If the length

of the pulse T_p is much shorter than T_1 and the radical decay is slow ($T_c \gg T_1$) then the absorption signal after the pulse is given by

$$\frac{M_Y(t)}{n_0 P_{eq}} = g_Y(t) \frac{P(I)}{P_{eq}} + G_Y(t) \frac{n(t)}{n_0} \left[1 + V(R) \frac{n_B(t)}{n_B(0)} \right] \quad (5.17)$$

where $n_0 = n(0)$ is the number of radicals produced by the pulse. The corresponding expression for a fast radical decay ($T_c \lesssim T_1$) is given in [XI]. The enhancement factor $V(R)$ is related to the recombination polarization P_a by

$$V(R) = P_a T_1 K_2 / P_{eq} = P_a T_1 / (P_{eq} T_{c2}) \quad (5.18)$$

where the second order decay constant K_2 is equal to

$$K_2 = T_{c2}^{-1} = k_2 F n_B(0). \quad (5.19)$$

The general form of the time dependent intensity curve follows from Eq.(5.17) and from the above comments on the time dependences of $g_Y(t)$ and $G_Y(t)$. The signal goes from zero to approximately $P(I)/P_{eq}$ in a time of order T_1 or ω_1^{-1} (which ever is shortest), then decays to $1+V$ during a time of order T_1 , and finally decays to zero during a time of order of the radical lifetime T_c . As $T_1/T_c \ll 1$ for a slow radical decay the enhancement $V(R)$ will most often be smaller than one.

If $|P(I)/P_{eq}| \gg 1$ the time dependence of the signal will be dominated by the fast growth to $P(I)/P_{eq}$ followed by the fast decay to $1+V=1$. This kind of time behaviour has been observed in many photolytic systems where the triplet mechanism has been active (see for example [24]) and it is illustrated in Fig. 19.

For radiolytic systems the initial polarization is zero except for secondary radicals which may have an initial

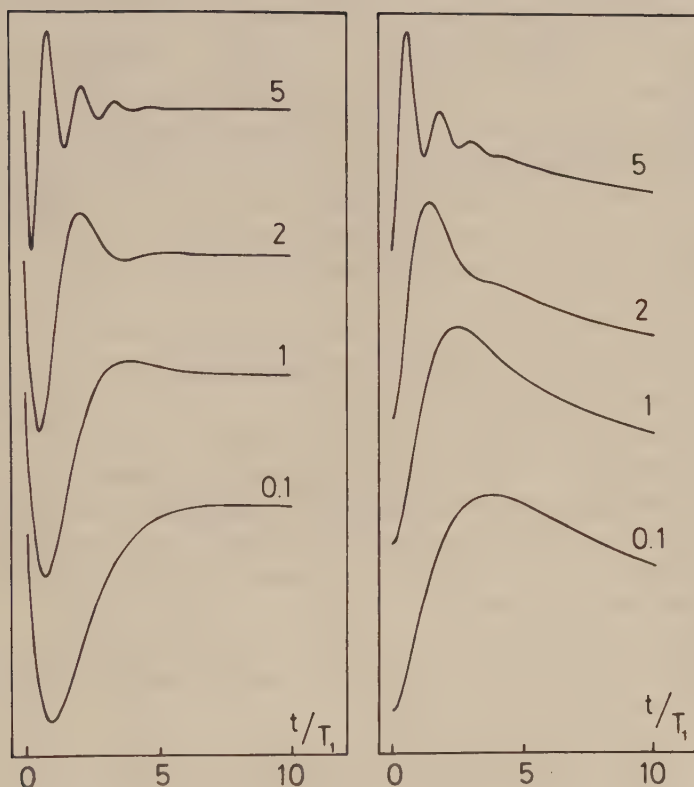


Fig. 19. Intensity versus time for a pulse experiment. The duration of the pulse is infinitely short and is applied at time zero. The intensity is zero at time zero and upwards corresponds to absorptive signals; the intensity scale is arbitrary and different curves have different scales. The curves are calculated by Eqs.(5.17) and (5.13). The left-hand figure is calculated for a system with initial polarization only and with $P(I)/P_{eq} = -10$. The right-hand figure is calculated for a system with recombination polarization only and with $V(R)=1$. Second order kinetics with $K_2 T_1 = 0.1$ has been used for both figures. The numbers on the curves refer to the values of $\omega_1 T_1$ used. Notice that the time interval shown is too short for all radicals to disappear and thus for the intensity to reach zero.

polarization transferred from the primary radical. The time dependence of the absorption signal is illustrated in Fig. 19. Many illustrative experimental curves may be found in [25].

It is observed from Fig. 19 that the time dependent intensity curves may show wiggles damping out in time. These wiggles have period $2\pi\omega_1^{-1}$ and represent the transient nutations of the magnetization which are damped by relaxation, cf. Eqs. (5.13). Therefore, they are only observed if $\omega_1 T_1 \gg 1$. The microwave field in the cavity has been determined from experimentally observed wiggles [24, 25].

5.5 Time resolved steady state experiments

In a time resolved steady state experiment the light source is modulated periodically and the periods are sufficiently long for a steady state to be reached in any period. This requires that the light intensity becomes constant in any period. A new period starts when the light intensity begins to change from the constant value.

It is shown in [XI] that the time dependence of the absorption signal is given by

$$M_Y(t) = M_Y^0 [g_z'(t) - g_Y(t)/(\omega_1 T_2)] + f(t) G_Y(t) \quad (5.20)$$

when the light source has rise and decay times much longer than T_1 . The beginning of any period is indicated by $t=0$ and M_Y^0 is the steady state value of the signal in the preceding period.

The steady state signal for a system exposed to a constant illumination can be obtained as the $t \rightarrow \infty$ limit of Eq.(5.20), with $k_0(t) = k_0$. The result is

$$M_Y(\text{steady state}) = n_0 P_{eq} G_Y^{(\infty)} T_1^{-1} [1 + V(I) + V(R)] \quad (5.21)$$

where n_0 is the steady state concentration of radicals. The

enhancements $V(I)$ and $V(R)$ are given by

$$V(I) = \frac{P(I) T_1 K}{P_{eq}} = \frac{P(I)}{P_{eq}} \frac{T_1}{T_c} \quad (5.22a)$$

$$V(R) = \frac{P_a T_1 K_2}{P_{eq}} = \frac{P_a}{P_{eq}} \frac{T_1}{T_{c2}} \quad (5.22b)$$

where the second order decay constant K_2 and the corresponding chemical lifetime T_{c2} are defined as

$$K_2 = \left. \frac{1}{n} \frac{dn}{dt} \right|_{k_2} (\infty) = k_2 F n_B (\infty) = T_{c2}^{-1} \quad (5.23a)$$

where ∞ indicates the steady state value. The total decay constant K is the sum of the decay constants for all individual processes depleting radicals evaluated at the steady state

$$K = T_c^{-1} = \frac{1}{n} \frac{dn}{dt} (\infty) = \sum_{\text{reaction } j} \left. \frac{1}{n} \frac{dn}{dt} \right|_j (\infty) = \frac{k_o}{n(\infty)} \quad (5.23b)$$

The prime indicates that only processes depleting radicals are included. For a pure first order reaction $K=k_1$, for a pure second order reaction $K=K_2$, and for a mixed first and second order reaction $K=K_1+K_2$.

The spin lattice relaxation time T_1 and the chemical lifetime T_c must be known in order to calculate the polarizations $P(I)$ and P_a from experimental values of the enhancements $V(I)$ and $V(R)$, cf. Eqs.(5.22). The lifetime of the radical may be obtained accurately from the time dependent intensity curves. However, the spin lattice relaxation time T_1 can be determined from the time dependent intensity curve only if T_1 (which is of order 1-10 μ s) is longer than the response time of the spectrometer. The accuracy by which the polarization can be determined is then mainly determined by the accuracy of T_1 . This accuracy may be as poor as a factor of two.

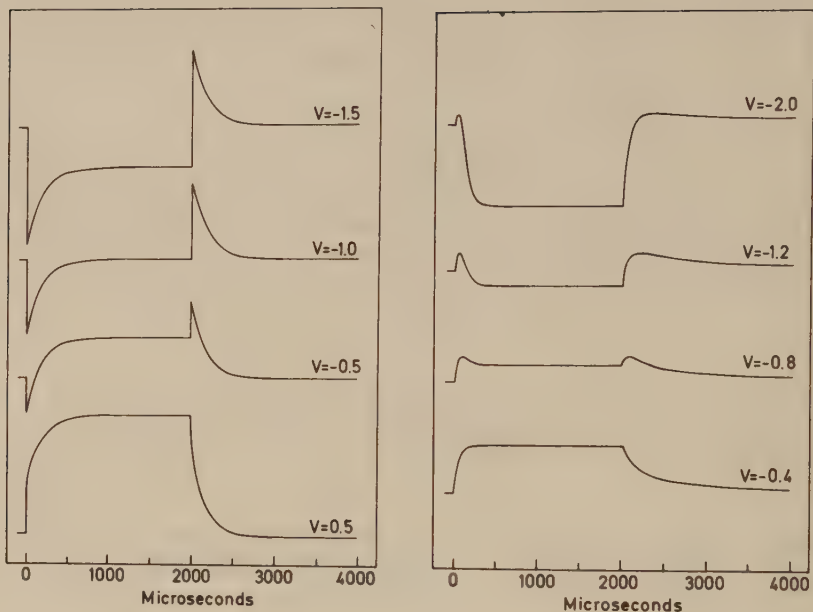


Fig. 20. Intensity versus time for a time resolved steady state experiments. The radical producing source, e.g. a light source, is assumed to have a constant power and to be turned on instantly at time zero and off instantly at 2000 μ s. Each curve corresponds to a different value of the enhancement V as indicated on the figure. The zero of intensity is defined by the value at time zero, upwards corresponds to absorption, and downwards to emission. The left-hand figure is calculated for a system satisfying first order kinetics and with initial polarization only, i.e. $V=V(I)$. The right-hand figure is calculated for a system satisfying second order kinetics and with recombination polarization only, i.e. $V=V(R)$. Other parameters used are $T_1=2\mu$ s and $T_c=120\mu$ s; T_c is the lifetime of radical defined in Eq.(5.23b). Notice that first order kinetics give identical decay rates in the two light periods, see e.g. the curve with $V=-1.0$ on the left-hand figure. Second order kinetics give rise to a faster decay in the light period, see e.g. the curve with $V=-0.4$ on the right-hand figure. From [III].

The smallest value of V that can be determined accurately by this type of experiment is of order 0.1. Thus a polarization ratio P/P_{eq} equal to 100 would require the lifetime of the radical to be less than $10^3 \times T_1 \approx 1 \text{ms}$ if the CIDEP effect should be observable.

It is most common to have two different time periods, called light and dark, in a time resolved steady state experiment. However, recently it has been found advantageous to use three [26]. In any case the time behaviour of the signal may be calculated from Eq.(5.20). Figure 20 illustrates the form of the curves for the two pure cases: (1) only $V(I) \neq 0$; (2) only $V(R) \neq 0$. It is observed that the pure initial polarization case can be distinguished from the case of recombination polarization. It is also observed by inspection of Fig. 20 that first order kinetics (left-hand figure) give identical decay rates in the two periods while second order kinetics (right-hand figure) give rise to a faster decay in the light period. Moreover, the sudden changes of the signal observed for the pure initial polarization case are of equal magnitude but opposite sign for the two periods. These observations may be helpful for a quick qualitative interpretation of experimental results.

Figure 21 displays an experimental time dependent intensity curve (full curve) from [VIII]. The sudden changes of the intensity indicate the presence of an initial polarization. However, the changes are not of equal magnitude and therefore recombination polarization may be present as well. Actually, the interpretation of the present curve is complicated by the fact that the light intensity is different from zero in the dark period; the light intensity in the dark period is the fraction ϵ^2 of the intensity in the light period and this gives rise to the approximate, relative values of the absorption signal indicated on the figure. Moreover, the "peak" in the light period is seen to be narrower than that in the dark period and this indicates second order kinetics. These qualitative conclusions are confirmed by a detailed

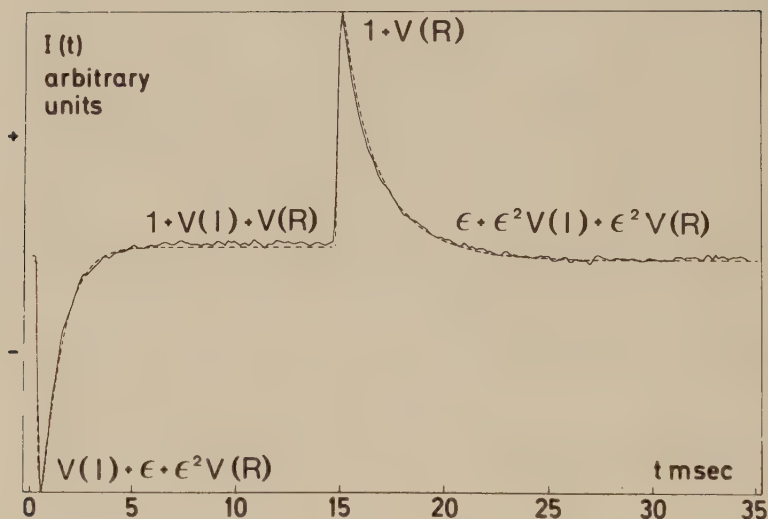


Fig. 21. Comparison of experimental and theoretical intensity curves for a time resolved steady state experiment. The experimental curve (full curve) is a time resolution of line 8 in Fig. 2. The sign convention of the intensity is + for absorption and - for emission. The radical producing source is a modulated xenon illuminator with rise and decay times about 25 μ s. The light intensity alternates between two constant values; the intensity in the "dark" period is the fraction ϵ^2 of the intensity in the "light" period. The "light" period starts at time zero and the "dark" period at 15 ms. The indicated relative values of the intensity may facilitate an analysis of the experimental curve. These values follow from Eqs.(5.20) - (5.23) and are exact for the two steady state values. However, the extreme values are accurate only when the lifetime of the radical is much longer than the spectrometer response time. The enhancements in the "light" period are denoted by $V(I)$ and $V(R)$ and are given by Eqs.(5.22) and 5.23). The response time of the spectrometer is 100 μ s. Other parameters used for the theoretical curve (broken curve) are $K=K_2=1.10 \times 10^3 \text{ s}^{-1}$ (i.e. $T_{c2}=0.91 \text{ ms}$), $V(I)=-0.66$, $V(R)=-0.05$, and $T_1 \approx 3 \mu\text{s}$. Due to the long response time the calculated curve is rather insensitive to the value of T_1 used. From [VIII].

curve fitting. The broken curve is calculated from Eq.(5.20) by using second order kinetics and by including initial polarization $V(I)$ as well as recombination polarization $V(R)$.

REFERENCES

1. R.W. Fessenden and R.M. Schuler, J.Chem.Phys. 39 2147 (1963).
2. J. Bargon, H. Fischer and U. Johnsen, Z.Naturf. 20a, 1551 (1967).
3. H.R. Ward and R.G. Lawler, J.Amer.Chem.Soc. 89, 5518 (1967).
4. G.L. Closs, J.Amer.Chem.Soc. 91, 4552 (1969); G.L. Closs and A.D. Trifunac, J.Amer.Chem.Soc. 92, 2183 (1970).
5. R. Kaptein and L.J. Oosterhoff, Chem.Phys.Letts. 4, 195 (1969); *ibid* 4, 214 (1969).
6. S.K. Wong, D.A. Hutchinson and J.K.S. Wan, J.Chem.Phys. 58, 985 (1973).
7. R. Kaptein, Chem.Comm. 732, (1971).
8. R.M. Noyes, Prog.React.Kinet. 1, 129 (1961).
9. F.J. Adrian, J.Chem.Phys. 53, 3374 (1970).
10. J.B. Pedersen, Chap. 17 in Ref. 27.
11. A.G. Redfield, Adv.Mag.Res. 1, 1 (1965).
12. J.B. Pedersen and P. Sibani, to be published.
13. A. Gierer and K. Wirtz, Z.Naturf. 8a, 532 (1953); see also A.H. Alwatter, M.D. Lumb and J.B. Birks, "Organic Molecular Photophysics" Chap. 8, editor J.B. Birks, J. Wiley & Sons (1973).
14. F.J. Adrian, J.Chem.Phys. 54, 3918 (1971).

15. G.T. Evans, P.D. Fleming and R.G. Lawler, J.Chem.Phys. 58, 2071 (1973)
16. A.J. Hoff, P. Gast and J.C. Romijn, FEBS Letts. 73, 185 (1977).
17. J.B. Pedersen, FEBS.Letts. , (1979).
18. R.W. Fessenden, J.Chem.Phys. 58, 2489 (1973).
19. A.D. Trifunac, J.Am.Chem.Soc., 98, 5202 (1976).
20. L.P. Hwang and J.H. Freed, J.Chem.Phys. 63, 4017 (1975).
21. P.W. Atkins, Chap. 10 in Ref. 27.
22. P.W. Atkins and G.T. Evans, Molec.Phys. 29, 921 (1975).
23. H.C. Torrey, Phys.Rev. 76, 1059 (1949).
24. P.W. Atkins, A.J. Dobbs and K.A. McLauchlan, Chem.Phys. Letts. 25, 105 (1974).
25. N.C. Verma and R.W. Fessenden, J.Chem.Phys. 65, 2139 (1976).
26. L.T. Muus, S. Frydkjaer and K. Bondrup Nielsen, Chem.Phys. 30, 163-168 (1978).
27. L.T. Muus, P.W. Atkins, K.A. McLauchlan and J.B. Pedersen (editors), "Chemically Induced Magnetic Polarization", D. Reidel Publ. Co., Dordrecht (1977).

APPENDIX I

Time scales of various processes

Process	Typical time scale (s)
Molecular tumbling	10^{-12} - 10^{-9}
Geminate recombination	10^{-10} - 10^{-7}
S-T _O mixing	10^{-8} - 10^{-7}
Electron T ₁ for triplets	10^{-10} - 10^{-8}
Electron T ₁ for radicals	10^{-6} - 10^{-5}
Nuclear T ₁ in radicals	10^{-5} - 10^{-3}
Nuclear T ₁ in products	1 - 30

APPENDIX II

Density, projection and superoperators

A quantum mechanical system is described by a state vector $|\psi\rangle$ which may be expanded in a complete orthonormal set $\{|n\rangle\}$

$$|\psi\rangle = \sum_n a_n |n\rangle, \quad \sum_n |a_n|^2 = 1. \quad (\text{A2.1})$$

For the state $|\psi\rangle$ the expectation value of an observable O is given by

$$\langle O \rangle = \langle \psi | O | \psi \rangle = \sum_n a_n a_m^* O_{mn} \quad (\text{A2.2})$$

where the asterisk indicates complex conjugation. Defining the density operator or density matrix of the system in state $|\psi\rangle$ as

$$\rho = |\psi\rangle\langle\psi|, \quad \rho_{nm} = a_n a_m^* \quad (\text{A2.3})$$

the above equations may be written as

$$\text{Tr} \rho = \sum_n \rho_{nn} = 1 \quad (\text{A2.4})$$

$$\langle O \rangle = \text{Tr}(\rho O) \quad (\text{A2.5})$$

where the trace operation is defined by the first equality in Eq. (A2.4). Consider now an ensemble of N identical systems, each described by a state vector $|\psi(v)\rangle, v=1, 2, \dots, N$. If all systems are in the same state $|\psi\rangle$ then the ensemble of systems is said to be in a pure state and may be described as indicated above for a single system. If the individual systems are not in identical states then the ensemble is said to be in a mixed state and the density matrix of the ensemble is defined as the ensemble average of the density matrices $\rho(v)$ of the individual systems (v)

$$\rho = N^{-1} \sum_{v=1}^N \rho(v) = N^{-1} \sum_{v=1}^N |\psi(v)\rangle\langle\psi(v)| \quad (\text{A2.6})$$

or in matrix form

$$\rho_{nm} = N^{-1} \sum_{v=1}^N a_n(v) a_m(v)^* \quad (A2.7)$$

Obviously, Eqs.(A2.4) and (A2.5) remain valid with ρ defined by Eq.(A2.6). In a representation that makes ρ diagonal

$$\rho_{nm} = w(n) \delta_{n,m} \quad , \quad \sum_n w(n) = 1 \quad (A2.8)$$

where $w(n)$ is the probability of finding a system in state $|n\rangle$. In this representation Eqs.(A2.5) and (A2.6) can be written in the transparent forms

$$\rho = \sum_n w(n) |n\rangle \langle n| \quad (A2.9)$$

$$\langle 0 \rangle = \sum_n w(n) 0_{nn} \quad (A2.10)$$

showing explicitly that a mixed state is a weighted mixture of pure states and that the average value of 0 consists of two types of averages: the quantum mechanical average given by 0_{nn} and the statistical average given by $w(n)$.

The projection operator P_n projecting on the state $|n\rangle$ is defined as

$$P_n = |n\rangle \langle n| \quad (A2.11)$$

Projection operators are idempotent, i.e. $P_n^2 = P_n$. Its effect on an arbitrary state $|\psi\rangle$ given by the linear combination (A2.1) is seen by the relation

$$P_n |\psi\rangle = |n\rangle \langle n | \psi \rangle = |n\rangle a_n \quad (A2.12)$$

Hence $\langle \psi | P_n | \psi \rangle = |a_n|^2$, i.e. the expectation value of P_n is the probability that the system is in state $|n\rangle$. Similarly, for a system in a mixed state the probability that the system is in state $|n\rangle$ is equal to

$$\text{Prob}\{|n\rangle\} = \langle P_n \rangle = \text{Tr}(\rho P_n) = \rho_{nn} \quad (A2.13)$$

The density matrix ρ is hermitian and in the Schrödinger picture satisfies the equation of motion

$$\partial \rho(t) / \partial t = -i H^\times \rho(t) = -i [H, \rho(t)] \quad (A2.14)$$

which follows from the time dependent Schrödinger equation

$$(\partial / \partial t) |\psi(t)\rangle = -i H |\psi(t)\rangle \quad (A2.15)$$

It is implied that the Hamiltonian is given in frequency units (rad/s). The superoperator H^x (also called the Liouville operator) is defined by the relation $H^x A = [H, A]$ for any operator A . A superoperator thus operates on an operator. The matrix form of Eq. (A2.15) is well known

$$(\partial/\partial t) a_n(t) = -i \sum_k H_{nk} a_k(t) \quad (A2.16)$$

or

$$(\partial/\partial t) \vec{\psi}(t) = -i \vec{H} \vec{\psi}(t) \quad (A2.17)$$

where $\vec{\psi}$ is defined by its components $\psi_n = \langle n | \psi \rangle = a_n$. Similarly, the equation of motion for ρ may be written in matrix form as

$$(\partial/\partial t) \vec{\rho}(t) = -i \vec{H}^x \vec{\rho}(t) \quad (A2.18)$$

$$(\partial/\partial t) \rho_{nm}(t) = -i \sum_{kl} (H^x)_{nm,kl} \rho(t)_{kl} = -i (H^x \rho(t))_{nm} \quad (A2.19)$$

The matrix elements of H^x are related to the matrix elements of H by the relation

$$(H^x)_{nm,kl} = \delta_{ml} H_{nk} - \delta_{nk} H_{lm}. \quad (A2.20)$$

It is important to notice that $\text{Tr} \rho$ is different from one and becomes time dependent when an operator annihilating particles is introduced in Eq. (A2.14), e.g. describing a chemical reaction cf. Eqs. (2.15) p.24. It follows from the above that ρ_{nn} is the probability of finding a system in state $|n\rangle$. Consequently, $\text{Tr} \rho(t)$ gives the probability that the particle is not annihilated at time t .

References:

- J. von Neumann, Nachr. Ges. Wiss. Götting, 1, 245, 273 (1927).
 P.A.M. Dirac, Camp. Phil. Soc. 25, 62 (1929).
 U. Fano, Rev. Mod. Phys. 29, 74 (1957)
 A readable presentation is given by L.T. Muus, Chap. 1 in "Electron Spin Relaxation in Liquids" (L.T. Muus and P.W. Atkins, editors) Plenum Press, 1972.

DANSK RESUMÉ

Nærværende afhandling er en sammenfatning af 11 tidligere publicerede artikler og udgør sammen med disse den for erhvervelse af den naturvidenskabelige doktorgrad indleverede afhandling. Afhandlingen omhandler kvantitative teoretiske beskrivelser af kemisk induceret magnetisk polarisation, CIDNP og CIDEP. Kemisk induceret magnetisk polarisation betegner de ikke-ligevægts populationer af elektronspin- og kernespin-tilstandene, der induceres af kemiske reaktioner. Den effekt, der vedrører kernespin-tilstandene, kaldes CIDNP. Den effekt, der vedrører elektronspin-tilstandene, kaldes CIDEP.

Kapitel 1 giver en introduktion til de behandlede fænomener, der manifesterer sig ved anormale NMR og ESR spektra. Disse anormale spektra kan f.eks. have nogle linier i emission og andre i forøget absorption, jvf. fig. 1. En forøgelse af absorptionsintensiteten med en faktor 1000 kan forekomme i NMR. Forøgelsen er mindre i ESR, jvf. fig. 2. Der er to mekanismer, der giver anledning til kemisk induceret magnetisk polarisation: radikalpar mekanismen og triplet mekanismen.

Ifølge radikalpar mekanismen kan kun produkter, der er afledt af en rekombinationsreaktion af et radikalpar, udvise CIDNP. Effekten fremkommer ved, at sandsynligheden for rekombinationen afhænger af radikalernes aktuelle kernespin-tilstand, jvf. fig. 3. Denne afhængighed af kernespin-tilstandene er indirekte. Den fremkommer ved, at rekombinations-sandsynligheden afhænger stærkt af den totale elektronspin-

tilstand af radikalparret (jvf. fig. 4), og at der findes en kernespinafhængig vekselvirkning (hyperfin vekselvirkningen), der inducerer overgange mellem de ureaktive og reaktive elektronspintilstande. Denne blanding af elektronspintilstandene foregår mest effektivt når radikalerne er adskilt. Mekanismen involverer derfor, at radikalerne mødes og reagerer, diffunderer fra hinanden og senere mødes igen, jvf. fig. 5.

De processer, der ifølge radikalpar mekanismen giver anledning til CIDEP, er illustreret i fig. 6. De er identiske med de processer, der gav anledning til CIDNP, bortset fra at den elektronspinselæktive rekombination af radikalerne erstattes af den effekt på den totale elektronspintilstand, der skyldes spin exchange vekselvirkningen.

Triplet mekanismen omhandler et radikalpar, der dannes ved en reaktion, der involverer et molekyle i en exciteret triplet tilstand. Sådanne reaktioner kan være en brintabstraktion eller en elektron-transfer reaktion. Den fundamentale antagelse i triplet mekanismen er, at en polarisation af elektronspinet i triplet molekylet vil overføres til de radikaler, der dannes ved reaktionen, jvf. fig. 7. En forklaring på, at et roterende triplet molekyle kan have en stærk anormal spinpolarisation, er mere kompliceret og diskuteres i kap. 4.

I kapitel 2 diskuteres forskellige aspekter af CIDNP. Der indledes med en kvalitativ udledning af nogle simple regler, der kan benyttes til en hurtig, kvalitativ analyse af eksperimentelle spektra. Denne udledning er tænkt som en indføring i de forskellige processer, der har betydning for CIDNP. Derefter omtales "reencounter" billedet, der beskriver den relative translatoriske diffusionsbevægelse ved en serie af efterfølgende kollisioner af de to radikaler. Denne beskrivelse har vist sig at være velegnet til CIDNP, og den benyttes i den efterfølgende generelle, kvantitative, teoretiske beskrivelse af CIDNP. Denne teori [IX,X] omtales forholdsvis detaillert, da den i forfatterens øjne er af central betydning. Denne teoretiske beskrivelse giver for praktisk taget alle systemer en nøjagtighed, der er på højde

med den nedenfor omtalte numeriske metode, som er eksakt for den antagne model. Anvendelsesområdet for den her omtalte teori er dog større end for den numeriske metode, idet den kan benyttes til systemer af langt større kvantemekanisk kompleksitet, og den udgør endvidere et naturligt udgangspunkt for udledning af tilnærmede, analytiske udtryk. Det karakteristiske ved denne generelle beskrivelse er, at beregningen af den komplicerede tidsudvikling af spinsystemet, der moduleres af diffusionsbevægelsen, er blevet opspaltet i en tidsuafhængig, kvantemekanisk beregning af spinsystemet og en tidsafhængig, stokastisk beregning af diffusionsbevægelsen.

Den almindeligst forekommende eksperimentelle situation falder ind under det såkaldte "højfelttilfælde", hvor Zeeman vekselvirkningen er meget større end hyperfin vekselvirkningen. For dette tilfælde kan den ovenfor nævnte teori benyttes til at udlede et sæt eksakte, generelle analytiske udtryk for CIDNP polarisationen. I disse udtryk, (2.43) indgår to uafhængige parametre Λ og F^* , der begge har værdier i intervallet $[0,1]$. Parameteren Λ angiver reaktiviteten af radikalparret og opfattes som en eksperimentel parameter, der er uafhængig af det anvendte magnetfelt. For et bestemt radikalpar afhænger Λ kun af temperaturen, viskositeten og ionstyrken af opløsningsmidlet. Den anden parameter (F^*) angiver hvor effektivt singlet og triplet (T_0) tilstandene blandes i den periode, hvori de to radikaler har kontakt med hinanden. Et analytisk udtryk, (2.44), for denne fundamentale parameter (F^*) er udledt. I dette udtryk indgår differensen mellem Larmor frekvenserne af de to radikaler, den rumlige udstrækning af exchange vekselvirkningen og sandsynlighedstætheden for førsteankomsttiden af diffusionsbevægelsen. Dette generelle udtryk er gyldigt for alle klassiske diffusionsmodeller. En beregning af F^* for et givet system er således reduceret til en beregning af ovennævnte sandsynlighedstæthed for dette system. For den kontinuerte, frie diffusionsmodel kan denne sandsynlighedstæthed beregnes analytisk, og F^* kan så beregnes ved brug af en lommeregner. For diffusion i et kraftfelt kan sandsynlighedstætheden beregnes ved hjælp af den nedenfor omtalte numeriske metode.

Kapitel 3 omhandler radikalpar modellen for CIDEF og indledes med en simpel teoretisk beskrivelse, der illustrerer effekterne af de involverede fysiske processer. Af kvantitative, teoretiske beskrivelser findes der i dag kun en, der kan benyttes for en vilkårlig r -afhængighed af exchange vekselvirkningen og for en generel diffusionsmodel. Denne beskrivelse benytter den stokastiske Liouville ligning, der løses ved hjælp af en endelig differenstechnik. Den blev oprindeligt benyttet til CIDEF [I], men er senere blevet benyttet til CIDNP [IV], liniebredde effekter fra Heisenberg spin exchange, og i en let modificeret form til intermolekylær dipol-dipol relaxation og til tidsforløbet af en kemisk reaktion i væsker. De væsentligste træk af denne teoretiske beskrivelse er omtalt her, medens der henvises til originalartiklerne, f.eks. [I], [II] eller [VII], for en mere detaljeret diskussion. Som eksempel på de nøjagtige (eksakte for den antagne model) numeriske resultater er valgt en grafisk præsentation af CIDEF polarisationens afhængighed af størrelsen af exchange vekselvirkningen. Denne afhængighed er væsentligt forskellig fra den fundet ved andre teorier. Kort fortalt vil de andre teorier forudsige en negligibel polarisation for systemer med en stærk exchange vekselvirkning, som f.eks. brint radikaler, hvorimod den her beskrevne teori vil forudsige en kraftig polarisation i overensstemmelse med de eksperimentelle resultater.

Triplet mekanismen for CIDEF er omtalt i kapitel 4. Som allerede nævnt fremkommer polarisationen af radikalerne ved en polarisationsoverførsel fra et molekyle i en exciteret, polariseret triplet tilstand. Figur 16 illustrerer de involverede fysiske processer, der er: excitation af et molekyle til en exciteret singlet tilstand efterfulgt af en anisotrop intersystem crossing til en triplet tilstand, fra hvilken molekylet reagerer kemisk, og hvorved der produceres to polariserede radikaler. Beskrivelsen af dette system kompliceres af, at triplet molekylet udfører en rotationsdiffusionsbevægelse, og at nogle af processerne beskrives lettest i molekylsystemet medens polarisationen skal udtrykkes i laboratoriesystemet. For at lette forståelsen af denne mekanisme er der inkluderet en

detailleret men simpel kvalitativ teoretisk beskrivelse, der ikke tidligere har været publiceret. Den kvantitative teori, der er udviklet i [VI], er her kun kort omtalt; den benytter den stokastiske Liouville ligning og løsningsmetoden er ekspansion i egenfunktioner. Denne teori kan benyttes til at udlede et approksimativt, analytisk udtryk for polarisationen, som er gyldigt når zero-field vekselvirkningen er mindre end Zeeman vekselvirkningen. Teorien kan også benyttes til at beregne nøjagtige numeriske resultater for vilkårlige værdier af de indgående parametre, hvilket for tiden ikke er muligt med andre metoder.

Kapitel 5 omhandler en teoretisk beskrivelse af tidsafhængigheden af de ESR signaler, der måles ved tidsopløst spektroskopi. Dette kapitel forbinder CIDEP polarisationen med de eksperimentelt observerbare størrelser. Den teoretiske beskrivelse bygger på Bloch ligningerne, der er et sæt tilnærmede bevægelsesligninger for magnetiseringen. Disse ligninger er blevet generaliseret til at inkludere polarisationsproduktion og kemiske processer [III] og [XI]. Den generelle form af løsningerne til disse ligninger er angivet, og der gives eksempler på løsninger for almindeligt forekommende eksperimentelle situationer. Disse eksemplificerede, generelle løsninger skulle lette en kvantitativ analyse af eksperimentelle data. For at lette en hurtig kvalitativ analyse af et eksperimentelt materiale er der inkluderet grafiske illustrationer (fig. 19 og 20) af tidsafhængigheden af ESR signalet for forskellige kombinationer af polarisationsproduktion og kinetik. Et eksempel på overensstemmelsen med eksperimentelle tidsafhængigheder er vist i fig. 21.

